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JOURNAL AND PROCEEDINGS
OF THE
ROYAL SOCIETY
OF NEW SOUTH WALES

FOR
1947
(INCORPORATED 1881)

VOLUME LXXXI —
Parts I-IV

EDITED BY
D. P. MELLOR, D.Sc.
Honorary Editorial Secretary

44811
THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE
STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN



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Issued as a complete volume, September 13, 1948.

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NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ _____ to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within _____ calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.]

PUBLICATIONS.

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862-5, pp. 374, out of print.		
Vols. I-XI	Transactions of the Royal Society, N.S.W., 1867-1877	„
Vol. XII	Journal and Proceedings	„ 1878, pp. 324, price 10s. 6d.
„ XIII	„ „ „ „	„ 1879, „ 255, „
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„ XV	„ „ „ „	„ 1881, „ 440, „
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LIST OF THE MEMBERS
OF THE
Royal Society of New South Wales
as at March 1, 1948

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

† Life Members.

Elected.

1944		Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney.
1938	P 2	†Albert, Adrien, Ph.D. <i>Lond.</i> , B.Sc. <i>Syd.</i> , A.R.I.C. <i>Gt. B.</i> , Commonwealth Research Fellow in Organic Chemistry, University of Sydney; p.r. "Greenknowe," Greenknowe-avenue, Potts Point.
1935		†Albert, Michel Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		†Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		†Alldis, Victor le Roy, I.S., Registered Surveyor, Box 57, Orange, N.S.W.
1909	P 12	†Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Camb.</i> , A.M.I.E. <i>Aust.</i> , Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1945		Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 2	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1946	P 1	Barclay, Gordon Alfred, Chemistry Department, Sydney Technical College, Harris Street, Ultimo, N.S.W.; p.r. 78 Alt Street, Ashfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1946	P 4	Beattie, Joan Marian (Mrs.), B.Sc., Box 92, P.O., Cobar.
1947		Beckmann, Peter, A.S.T.C., Chemist, Staff Hostel, Glen Davis, N.S.W.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. (<i>Oxon.</i>), 6 Beechcroft-road, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 26A Wolseley-road, Mosman.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills.
1946		Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carabella-street, Kirribilli.
1933	P 28	Bolliger, Adolph, Ph.D., F.A.C.I., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.)
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., International Wool Secretariat, Dorland House, 18 Regent-street, London, S.W.1. (President, 1935.)
1939	P 15	Bosworth, Richard Charles Leslie, M.Sc., D.Sc. <i>Adel.</i> , Ph.D. <i>Camb.</i> , F.A.C.I., F.Inst.P., c/o C.S.R. Co. Ltd., Pyrmont; p.r. 41 Spender-road, Killara.
1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney; p.r. 19 Handley-avenue, Thornleigh.

Elected.

- 1946 Breyer, Bruno, M.D., Ph.D., M.A., Lecturer in Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Sydney.
- 1940 Bridgen, Alan Charles, B.Sc., 8 Clifford-avenue, Manly.
- 1919 P 1 Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
- 1942 Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
- 1935 P 4 Brown, Ida Alison, D.Sc., Lecturer in Palaeontology, University of Sydney.
- 1945 Brown, Norma Dorothy (Mrs.), B.Sc., Biochemist, 58 Hopetoun-avenue, Vacluse, N.S.W.
- 1941 Brown, Samuel Raymond, A.C.A. Aust., 87 Ashley-street, Chatswood.
- 1913 P 22 †Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
- 1947 Buchanan, Gregory Stewart, B.Sc. (Hons.), Lecturer in Physical Chemistry, Sydney Technical College; p.r. 51 Argyle-street, Ryde, N.S.W.
- 1940 Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
- 1946 Bullen, Keith Edward, M.A., B.Sc. N.Z., M.A. Melb., Ph.D., Sc.D. Camb., Professor of Applied Mathematics, University of Sydney, Sydney, N.S.W.
- 1898 †Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. Syd., F.R.A.C.S., "Radstoke," Elizabeth Bay.
- 1926 Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
- 1940 P 1 Cane, Reginald Frank, D.Sc., A.A.C.I., General Motors-Holdens Ltd., Fishermen's Bend, Melbourne, Victoria; p.r. 2 David-street, St. Kilda, S.2.
- 1940 Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
- 1938 P 2 Carey, Samuel Warren, D.Sc., Professor of Geology, University of Tasmania, Tasmania.
- 1903 P 5 †Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
- 1945 Carter, Harold Burnell, B.V.Sc., Research Officer, C.S.I.R., McMaster Laboratory; p.r. Flat 4, 13 Milson-road, Cremorne.
- 1944 Cavill, George William Kenneth, M.Sc., c/o Department of Organic Chemistry, The University, Liverpool, Great Britain.
- 1913 P 4 †Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
- 1933 Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
- 1940 Chambers, Maxwell Clark, B.Sc., c/o Coty (England) Ltd., 35-41 Hutchinson-street, Moore Park; p.r. 58 Spencer-road, Killara.
- 1913 P 21 †Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
- 1935 P 2 Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
- 1935 Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
- 1938 Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vacluse.
- 1941 Cohen, Max Charles, B.Sc., A.I.F., 80 "St. James," Stanley-street, Sydney.
- 1940 Cohen, Samuel Bernard, M.Sc., A.A.C.I., 34 Euroka-street, Northbridge.
- 1940 P 3 Colditz, Margaret Joyce, M.Sc., 9 Beach-street, Kogarah.
- 1940 P 2 Cole, Edward Ritchie, B.Sc., 7 Wolsten-avenue, Turramurra.
- 1940 P 1 Cole, Joyce Marie, B.Sc., 7 Wolsten-avenue, Turramurra.
- 1940 Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
- 1946 Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield.
- 1920 Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
- 1945 Coombes, Arthur Roylance, A.S.T.C. (chem.), 14 Georges River-road, Croydon.
- 1913 P 5 †Coombes, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
- 1933 Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
- 1937 P 8 Cornforth, Rita Harriet, D.Phil. (Oxon.), M.Sc. (Syd.), c/o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
- 1940 Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
- 1919 Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
- 1909 P 7 †Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
- 1941 P 1 Craig, David Parker, Lecturer in Inorganic Chemistry, University of Sydney; p.r. 62 Springdale Rd., Killara.

Elected.

1921	P 1	†Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay ; p.r. 101 Villiers-street., Rockdale.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1947		Curry, Gladys Olive (Mrs.), B.Sc. <i>Melb.</i> , F.R.I.C. <i>Gt. B.</i> , A.A.C.I., Director of Research, Australian Leather Research Association ; p.r. "Cahors," No. 75, 117 Macleay-street, Pott's Point, N.S.W.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		†Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
1906		†Dixon, Sir William, "Merridong," Gordon-road, Killara.
1913	P 3	†Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney ; p.r. 18 Hillview-street, Sans Souci.
1946		Donohoo, Norma Winifred, B.Sc., 41 Second-street, Ashbury.
1947		Downes, Alan Marchant, B.Sc. (Hons.), Railway-parade, Glenfield.
1943		Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
1937	P 10	Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney ; p.r. 40 Manning-road, Double Bay. (President, 1947.)
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney ; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 39	Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney, Sydney.
1945		Eade, Ronald Arthur, B.Sc., 13 Steward-street, Leichhardt.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
1940		Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
1937		English, James Roland, L.S., Sydney.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland ; p.r. Regent-street, West Maitland.
1944		Erhart, John Charles, Chemical Engineer, c/o "Ciba" Coy., Basle, Switzerland.
1908		†Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. <i>Lond.</i> , A.R.A.I.A., 6 Major-street, Coogee.
1944		Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 338 Chapple-street, Broken Hill.
1939		Faull, Norman Augustus, B.Sc., A.Inst.P., c/o National Standards Laboratory, University Grounds, City-road, Chippendale
1909	P 7	†Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
1940		Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1933		Fletcher, Harold Oswald, Paleontologist, Australian Museum, College-street, Sydney.
1879		†Foreman, Joseph, M.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Edin.</i> , "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
1905		†Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1943		Frederick, Robert Desider Louis, B.E., 162 Buckley-street, Essendon, W.5, Victoria.
1940		Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
1944	P 2	Friend, James Alan, 16 Kelburn-road, Roseville.
1945		Furst, Hellmut Friedrich, B.D.S. (<i>Syd.</i>), D.M.D. (<i>Hamburg</i>), Dental Surgeon, 158 Bellevue-road, Bellevue Hill.
1935	P 2	Garretty, Michael Duhan, D.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney ; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.

Elected.

1942	P 3	Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
1947		Gill, Naida Sugden (Miss), B.Sc., 45 Neville-street, Marrickville.
1947		†Gill, Stuart Frederic, School Teacher, 45 Neville-street, Marrickville.
1940		Gillis, Richard Galvin, 4 Tennyson-avenue, Caulfield, S.E.7, Victoria.
1945		Goddard, Roy Hamilton, F.C.A. Aust., Royal Exchange, Bridge-street, Sydney.
1947		Goldsworthy, Neil Ernest, M.B., Ch.M. Syd., Ph.D., D.T.M. & H. Camb., D.T.M. & H. Eng., D.P.H. Camb., 65 Roseville-avenue, Roseville.
1936		Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill.
1940		Graves, John Nevil, B.Sc., c/o Mr. R. Clarke, Ontava Ave., West Pennant Hills.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
1946		Gutmann, Felix, Ph.D., Commonwealth Research Fellow, Faculty of Agriculture, University of Sydney, Sydney.
1947		Hall, Lennard Robert, B.Sc., Geological Survey, Department of Mines, Bridge-street, Sydney.
1945		Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, 15A Wharf-road, Longueville.
1892		†Halloran, Henry Ferdinand, L.S., A.M.I.E. Aust., F.S.I. Eng., M.T.P.I. Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill.
1940	P 9	Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney.
1905	P 6	†Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
1936		Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
1934		Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1946		Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney.
1929		Hawley, J. William, J.P., Financial Agent.
1934		Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 34 Nicholson-street, Chatswood.
1919		Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1945		Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd.; p.r. 10 Cremorne-road, Cremorne.
1938	P 4	Hill, Dorothy, M.Sc. Q'ld., Ph.D. Cantab., Geological Research Fellow, University of Queensland, Brisbane.
1946		Hinder, Nora (Miss), B.Sc. Syd., 22 Chester-street, Epping.
1936		Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
1928		Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), "St. Cloud," Beaconsfield-road, Chatswood.
1916		Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, 81 Frederick-street, Rockdale.
1941		Howard, Harold Theodore Clyde, B.Sc., Principal, Technical College, Granville.
1935		Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
1938	P 8	Hughes, Gordon Kingsley, B.Sc., Department of Chemistry, University of Sydney, Sydney.
1947		Humpoletz, Justin Ernst, B.Sc. Syd., 21 Belgium-avenue, Roseville.
1923	P 3	†Hynes, Harold John, D.Sc., B.Sc. Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
1943		Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville.
1942	P 1	Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
1940		Johns, Thomas Harley, M.Sc., 130 Smith-street, Summer Hill.
1946		Johnson, Guy Frederick, 644 Botany-road, Alexandria.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)

Elected.

1935	P 6	Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1935		Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
1940		Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
1924	P 1	Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove.
1943		Kimble, Jean Annie, Research Chemist, B.Sc., 383 Marrickville-road, Marrickville.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.
1939	P 1	Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., Scientific Liaison Officer, Victoria Barracks, Melbourne, Victoria.
1946		Lederer, Michael, 67 Edgecliff-road, Bondi Junction.
1947		Le Fevre, Raymond James Wood, D.Sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney.
1936	P 2	Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 56	†Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.)
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 3	Lipson, Menzie, B.Sc., A.A.C.I., Chemist, c/o Department of Textile Industry, Leeds University, Leeds 2, England.
1947		Lloyd, James Charles, B.Sc. Syd., N.S.W. Geological Survey, 41 Goulburn-street, Liverpool.
1940	P 1	Lockwood, William Hutton, B.Sc., Food and Agricultural Division, Control Commission for Germany (B.E.), Berlin, B.A.O.R., Germany.
1906		†Loney, Charles Augustus Luxton, M.Am.soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1943		†Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park.
1945		Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 84 Marine-parade, Maroubra.
1939	P 4	Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1.
1943		McCoy, William Kevin, Analytical Chemist, R.A.A.F.; p.r. 16 Bishop's-avenue, Randwick.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	†McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	†McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P 7	McKenzie, Hugh Albert, B.Sc., Assistant Research Officer, C.S.I.R.; p.r. 52 Bolton-street, Guildford.
1943		McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Technological Museum, Harris-street, Ultimo; p.r. 14 Orwell-street, Potts Point.
1932		McKie, Rev. Ernest Norman, B.A. Syd., St. Columba's Manse, Guyra.
1947		McMahon, Patrick Reginald, M.Agr.Sc. N.Z., Ph.D. Leeds, A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney.
1927		McMaster, Sir Frederick Duncan, kt., "Dalkeith," Cassilis, N.S.W.
1943		McNamara, Barbara Joyce (Mrs.), M.B., B.S., Dimbulah, North Queensland.
1946		McPherson, John Charters, "Greenleys," No. 6 Wallarings-avenue, Neutral Bay.
1946	P 1	McRoberts, Helen May, B.Sc., New England University College, Armidale.
1947		Magee, Charles Joseph, D.Sc.Agt. Syd., M.Sc. Wis., Chief Biologist, Department of Agriculture; p.r. 4 Alexander-parade, Roseville.

Elected.

- 1945 Makepeace, Barbara (Mrs.), B.Sc., Biochemist, 5 Jenkin-street, Chatswood.
 1947 Maley, Leo Edmund, B.Sc. (Hons.), 116 Maitland-road, Mayfield
 1940 Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
 1947 Mapstone, George E., M.Sc., A.A.C.I., M.Inst.Pet., Chief Chemist of National Oil
 Pty. Ltd., Glen Davis; p.r. 2 Anderson Square, Glen Davis, N.S.W.
 1944 Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
 1946 May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill.
 1935 P 1 Maze, Wilson Harold, M.Sc., Deputy Registrar, University of Sydney, Sydney.
 1912 †Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University
 Grounds, Newtown; p.r. 98 Sydney-road, Manly.
 1939 P 24 Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, Uni-
 versity of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President,
 1941-42.)
 1941 Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd.,
 Loftus-street, Arncliffe.
 1940 Mercer, Edgar Howard, Textile Department, University of Leeds, Leeds,
 England.
 1928 Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, "Walla Walla,"
 Hull-road, Beecroft.
 1940 Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd.
 15 Shaw-avenue, Earlwood.
 1943 Molloy, Ernest Patrick, Assistant Sectional Manager, 129 Gibbes-street,
 Rockdale.
 1945 Morris, Samuel, A.S.T.C. (Chem.), A.A.C.I., F.C.S.G.B., 217 Burns Bay-road, Lane
 Cove.
 1941 Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
 1922 P 27 Morrison, Frank Richard, A.A.C.I., F.C.S., Economic Chemist, Museum of
 Technology and Applied Science, Harris-street, Ultimo.
 1934 Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
 1944 Moye, Daniel George, Chemist, Warragamba Dam.
 1946 Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney.
 1915 Murphy, Robert Kenneth, Dr.Eng., Chem.Eng., A.S.T.C., M.I.Chem.E., F.A.C.I.,
 Principal, Sydney Technical College, Sydney.
 1923 P 2 Murray, Jack Keith, B.A., B.Sc.Agr., Government House, Port Moresby, Papua.
 1930 P 6 Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.T.P., Lecturer in
 Philosophy and Psychology, University of Queensland, Brisbane, Qld.
 1943 Neuhaus, John William George, 190 Old Prospect-road, Wentworthville.
 1932 Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Botany,
 Victoria University College, P.O. Box 1580, Wellington, N.Z.
 1943 Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal
 Glass Co.; p.r. No. 2 Flat, corner Hendy-avenue and Rainbow-streets,
 Coogee.
 1935 Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
 1945 P 1 Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra,
 A.C.T.
 1938 P 1 Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., c/o C.S.I.R., 314 Albert-street,
 East Melbourne, Vic.
 1920 P 4 †Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of
 Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road,
 Lindfield. (President, 1934.)
 1947 Nordon, Peter, A.S.T.C., A.A.C.I., Chemical Engineer, 1 Edgecliff-road, Bondi
 Junction.
 1940 P 25 Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
 1935 P 4 O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory,
 Sydney.
 1947 Old, Adrian Noel, B.Sc.Agr., Chemist, Department of Agriculture; p.r. 4 Spring-
 field-avenue, Pott's Point.
 1921 P 6 Osborne, George Davenport, D.Sc. Syd., Ph.D. Camb., Lecturer and Demonstrator
 in Geology in the University of Sydney. (President, 1944.)
 1920 P 74 Penfold, Arthur Ramon, F.A.C.I., F.C.S., Director, Museum of Technology and
 Applied Science, Harris-street, Ultimo. (President, 1931.)
 1938 Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
 1935 Phillips, Orwell, 55 Darling Point-road, Edgecliff.

Elected.

- 1946 Pinwell, Norman, B.A. (*Q'land*), The Scots College, Bellevue Hill.
- 1943 Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
- 1919 Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
- 1896 †Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
- 1946 Potter, Bryce Harrison, B.Sc. (Hons.) (*Syd.*), 13 Fuller's-road, Chatswood.
- 1921 P 2 Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
- 1938 Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
- 1945 Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst.
- 1927 Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
- 1918 P 1 Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
- 1945 Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood.
- 1893 †Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
- 1935 P 3 †Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
- 1922 P 6 Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
- 1940 P 2 Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
- 1919 P 3 Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
- 1936 Randall, Harry, Buena Vista-avenue, Denistone.
- 1947 Ray, Nancy Evelyn (Mrs.), Plastics Manufacturer, 14 Hedger-avenue, Ashfield.
- 1947 Ray, Reginald John, Plastics Manufacturer and Research Chemist, 14 Hedger-avenue, Ashfield.
- 1931 P 1 Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, Vic.
- 1935 Reid, Cicero Augustus, 19 Newton-road, Strathfield.
- 1947 Reuter, Fritz Henry, Ph.D. (*Berlin*, 1930), F.A.C.I., 94 Onslow-street, Rose Bay.
- 1946 Rhodes-Smith, Cecil, 261 George-street, Sydney.
- 1947 Ritchie, Arthur Sinclair, A.S.T.C., Lecturer in Mineralogy and Geology, Newcastle Technical College; p.r. 188 St. James-road, New Lambton, N.S.W.
- 1947 Ritchie, Bruce, B.Sc. (Hons.), c/o Pyco Products Pty. Ltd., 576 Parramatta-road, Petersham.
- 1939 P 15 Ritchie, Ernest, M.Sc., Senior Lecturer, Chemistry Department, University of Sydney, Sydney.
- 1939 P 3 Robbins, Elizabeth Marie (Mrs.), M.Sc., 36 Cambridge-street, Epping.
- 1933 Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
- 1940 Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush; p.r. Flat 4, 43 Johnston-street, Annandale.
- 1935 P 2 Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
- 1940 Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
- 1940 Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
- 1945 Rountree, Phyllis Margaret, M.Sc. *Melb.*, Dip.Bact. *Lond.*, 25 Elizabeth Bay-road, Elizabeth Bay.
- 1945 Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory; p.r. 83 Woniara-road, Hurstville.
- 1945 Sampson, Aileen (Mrs.), Sc.Dip. (A.S.T.C., 1944), 9 Knox-avenue, Epping.
- 1935 Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
- 1941 P 3 Sawkins, Dansie Thomas, M.A. *Syd.*, B.A. *Camb.*, 60 Boundary-street, Roseville.

Elected.

1920		Scammell, Rupert Boswood, B.Sc. <i>Syd.</i> , A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1946	P 1	Scott, Beryl (Miss), B.Sc., 314 Rowe-street, Eastwood.
1940		Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, c/o Shell Co. of Aust., 163 William-street, Melbourne, C.I., Vic.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. <i>Melb.</i> , 43 Robertson-road, Centennial Park.
1945		Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1945	P 2	Simmons, Lewis Michael, B.Sc. (Hons.) <i>Lond.</i> , Ph.D. <i>Lond.</i> , F.A.C.I., Head of Science Department, Scots College; p.r. The Scots College, Victoria-road, Bellevue Hill.
1943		Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiaatea," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, New College, Oxford, England.
1947		Smith-White, William Broderick, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , Department of Mathematics, University of Sydney; p.r. 7 Henson-street, Summer Hill.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboono," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	†Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney; p.r. 79 Ocean-street, Woollahra.
1940		Stroud, Richard Harris, B.Sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.
1918		†Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1919		†Sutherland, George Fife, A.R.C.Sc. <i>Lond.</i> , Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. <i>Melb.</i> , B.Sc. <i>Ozon.</i> , Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. <i>Adel.</i> , c/o Technical Service Department, ICIANZ, Box 1911, G.P.O., Melbourne, Victoria.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Squadron Leader, R.A.A.F., M.Sc., A.Inst.P. 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic.
1946		Thomas, Ifor Morris, M.Sc., Department of Zoology, University of Adelaide, Adelaide, S.A.
1919		Thorne, Harold Henry, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.
1923		Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
1943		Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.

Elected.

1940		Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 10	†Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney; p.r. "Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.)
1943		Walker, James Foote, Company Secretary, 11 Bruce-dale-avenue, Epping.
1919	P 2	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1945		Walters, Laurence Gordon, B.Sc., Flat 3, 33 Gould-street, Bondi.
1913	P 5	†Wardlaw, Hy. Sloane Halero, D.Sc. <i>Syd.</i> , F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1944		Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T.
1921		†Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett, Illoura-avenue, Wahroonga.
1919	P 1	Waterhouse, Lionel Lawry, B.E. <i>Syd.</i> , Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 7	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor of Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1944		Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney.
1941	P 1	Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
1911	P 1	†Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 6 Collingwood-street, Drummoyne.
1947		Webb, Gordon Keyes, A.F.I.A., A.C.I.S., Accountant, c/o Max Wurcker (1930) Pty. Ltd., 99 York-street, Sydney.
1945		Webster, Evelyn May, B.Sc., Chemist, 2 Buena Vista-avenue, Mosman.
1920		Wellish, Edward Montague, M.A., Emeritus Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1947		Werner, Ronald Louis, Industrial Chemist, 25 Dine-street, Randwick.
1946		Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill.
1909	P 3	†White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1943		Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., c.o. Davis Gelatine (Aust.) Pty. Ltd., Spring-street, Botany.
1944	P 1	Willis, John Bryan, B.Sc., Demonstrator in Chemistry, University of Sydney; p.r. Flat 2, Russell Hall, 17 Mount Street, Coogee.
1945		Willis, Jack Lehano, B.Sc., Flat 5, "Narooma", Hampden-street, North Sydney.
1943		Winch, Leonard, B.Sc., 60 Baldwin-avenue, Asquith.
1940		Wogan, Samuel James, Range-road, Sarina, North Queensland.
1936	P 5	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Government Astronomer, Sydney Observatory, Sydney.
1906	P 12	†Woolnough, Walter George, D.Sc., F.G.S., c/o Mr. W. L. Woolnough, "Callabonna", 8 Park-avenue, Gordon.
1916		Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 7 Wynyard-street, Sydney.
1946		Wyndham, Norman Richard, M.D., M.S. (<i>Syd.</i>), F.R.C.S. (<i>Eng.</i>), F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turrumurra.

HONORARY MEMBERS.

Limited to Twenty.

Elected.

1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1946	Jones, Sir Harold Spencer, M.A., D.Sc., F.R.S., Astronomer Royal, Royal Observatory, Greenwich, London, S.E.10.
1915	Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912	Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.
1946	Wood-Jones, F., D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (Lond.), F.R.S., F.Z.S., Professor of Anatomy, University of Manchester, England.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
- "The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
- "Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
- "The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E. D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.
1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.
1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.
1947. "The Teachers of Geology in Australian Universities." By Professor H. S. Summers, D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

- 1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 *George Bentham, C.M.G., F.R.S.
- 1880 *Professor Thos. Huxley, F.R.S.
- 1881 *Professor F. M'Coy, F.R.S., F.G.S.
- 1882 *Professor James Dwight Dana, LL.D.
- 1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

Awarded.

- 1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
 1886 *Professor L. G. De Koninck, M.D.
 1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
 1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
 1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
 1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
 1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
 1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
 1893 *Professor Ralph Tate, F.L.S., F.G.S.
 1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
 1895 *Robert Etheridge, Jnr.
 1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
 1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
 1901 *Edward John Eyre.
 1902 *F. Manson Bailey, C.M.G., F.L.S.
 1903 *Alfred William Howitt, D.Sc., F.G.S.
 1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
 1909 *Dr. Walter E. Roth, B.A.
 1912 *W. H. Twelvetrees, F.G.S.
 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
 1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
 1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
 1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
 1920 *Joseph Edmund Carne, F.G.S.
 1921 *Joseph James Fletcher, M.A., B.Sc.
 1922 *Richard Thomas Baker, The Crescent, Cheltenham.
 1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
 1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
 1925 *Charles Hedley, F.L.S.
 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
 1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
 1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
 1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
 1935 *George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
 1938 *Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
 1939 *C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
 1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.
 1945 Professor William Noel Benson, B.A., D.Sc., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.
 1946 Black, J. M., A.L.S. (*honoris causa*), Adelaide, S.A.
 1947 *Hubert Lyman Clark, A.B. D.Sc., Ph.D., Hancock Foundation, U.S.C., Los Angeles, California.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
 1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
 1938 Frank Macfarlane Burnet, M.D. (Melb.), Ph.D. (Lond.), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
 1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.
 1947 John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
1940 G. J. Burrows, B.Sc., University of Sydney.
1942 J. S. Anderson, B.Sc., Ph.D. (Lond.), A.R.C.S., D.I.C., University of Melbourne.
1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.
1946 Briggs, L. H., D.Phil. (Oxon.), D.Sc. (N.Z.), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.
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14 JAN 1948

PRESIDENTIAL ADDRESS

By F. LIONS, B.Sc., Ph.D.

Delivered before the Royal Society of New South Wales, April 2, 1947.

PART I. GENERAL.

Ladies and Gentlemen :

The stated aim of the Royal Society of New South Wales is " to encourage studies and investigations in, and to receive at its stated meetings, and to publish, original papers on Science, Art, Literature and Philosophy, and especially on such subjects as tend to develop the resources of Australia, and to illustrate its natural history and productions ".

As evidence of the efforts of the Society to live up to its aim, I have to report that 22 papers were accepted for reading and publication during the year, a pleasing feature being the variety of the subjects considered. This total does not nearly approach the record number of 50 papers read in the 1937-38 period, neither does it show any increase on the number presented last year. It might have been expected that the cessation of war would have led to a much greater volume of published work, but it must be remembered that the war effort required of the universities and technical colleges will not be completed for some years yet. When the strain of the excessive teaching duties imposed on the staffs of educational institutions has eased, it is confidently expected that their research output will again increase.

It takes very little consideration, too, to realise that a spate of papers embodying the results of completed researches will eventuate, because although the teaching strain at the moment is well-nigh intolerable, a record number of students is being initiated into the methods of science, and undoubtedly many of them will soon be able and eager to carry out original research work. Much of it should be published in the Society's Journal, but I cannot too strongly emphasise to the Society that now is the time to interest these embryo scientists in the work of this oldest scientific society in the State.

There is still a time lag in the publication of the Journal. Efforts are being made to get it printed and issued on the due dates, but the very great difficulties which beset the printing trade in this State at present militate against such a desirable result. The Council is properly concerned about the delays and is constantly endeavouring to accelerate publication. It should be pointed out to authors that they can assist very materially by correcting proofs promptly and returning them without delay to the editorial secretary.

During 1946 Lieutenant-General John Northcott, C.B., M.V.O., Commander-in-Chief of the British Commonwealth Forces of Occupation in Japan, was commissioned by His Majesty the King as Governor of New South Wales. He has been graciously pleased to accept the office of Patron of our Society, and the Society was honoured by his presence, together with that of his daughter, Miss Northcott, at the Society's Annual Dinner, which was held in the Sydney University Union Withdrawing Room on March 27th, 1947, and was well attended. The Society was also honoured by the presence of the Minister for Education, Mr. R. J. Heffron, and his wife, and there were many other

A—April 2, 1947.

guests. The function was of a high standard and was greatly enjoyed by all those who attended.

At the present time there are 314 ordinary members of the Society, and, with the two honorary members you have just elected, five honorary members. During the year we lost seven members by resignation and three by death. Twenty-two new members were elected during the year.

The attendance at our monthly meetings has been satisfactory, averaging 37, but with the passing of war-time and immediate post-war restrictions it is hoped that there will be even greater attendances at the ordinary monthly meetings. At these meetings the device of supplementing the reading of papers with exhibits, the screening of a film ("Eruption of Ruapehu") and lecturettes was again followed. In all, five lecturettes were given: by Mr. Chalmers ("Australian Gem Stones"), Dr. Mellor ("Synthetic Diamonds" and "New Instruments of Scientific Interest"), Dr. Still ("Some Recent Advances in Cellular Metabolism"), and Mr. Le Souef ("Consciousness and Instinct"). Mr. Faull exhibited a Geiger counter at the December meeting.

The Council has made strong representations to the Science House management committee for the installation of modern projection equipment in the main hall of Science House. Such equipment is now readily available from America, and, as those who attended last year's symposium on visual education methods must appreciate, its use could add considerably to the instruction and enjoyment of members and would undoubtedly increase the attendances at our monthly meetings.

Two symposia were held during the year, and proved to be very popular. The first was on "Energy Resources of the Commonwealth", the speakers being Dr. Dulhunty ("Fuel Energy"), Dr. Iredale ("Solar Energy") and Dr. Makinson ("Atomic Energy"). The second symposium dealt with "Tracer Elements", the speakers being Mr. Faull ("The Production and Measurement of Radio active Isotopes") and Dr. Rogers ("The Use of Radioactive Tracers in Biological Investigations").

The November meeting of the Society was devoted to a commemoration of great scientists, the speakers being Professor Elkin ("Boucher de Perthes—The Antiquity of Human Culture"), Mr. Smith-White ("Gottfried Wilhelm Leibnitz"), Mr. Wood ("Tycho Brahe") and Dr. Albert ("Valerius Cordus and the Pharmacopœia").

During the year five popular science lectures were given, the speakers being Mr. Fletcher ("Extinct Monsters"), Professor O'Neill ("A New Road for the Disabled Soldier"), Mr. Penfold ("Recent Developments in Plastics"), Miss Rountree ("The Smallest Forms of Life-Virus") and Dr. Hotten ("Triumph over Pain—The Story of Anæsthesia").

This year the Clarke Memorial Lecture was delivered by Professor L. A. Cotton, who chose as his subject "The Pulse of the Pacific". Despite the fact that on the night of the lecture the weather was appalling and that transport services were heavily restricted, he had a large and appreciative audience who, in turn, were amply rewarded by a most excellent lecture.

The Clarke Memorial Medal was awarded to Mr. J. M. Black, A.L.S. (*honoris causa*), of Adelaide, in recognition of his distinguished contributions to natural science in Australia. At the request of the Society the Medal was presented to Mr. Black by the President of the Royal Society of South Australia in Adelaide on Thursday, April 11th, 1946.

During 1946 Dr. L. H. Briggs, of Auckland University College, was invited to deliver the Liversidge Research Lectures. He chose as his subject "Plant Products of New Zealand", and delivered two very stimulating lectures. The importance of intensive plant product research in Australia was brought home during the war when it was shown that in certain species of *Duboisia* Australia

possessed some of the world's best sources of the alkaloids hyoscyne and hyoscyamine. Much the same position obtains now with respect to the glucoside rutin, which has been found to be of value in the treatment of capillary fragility associated with hypertension. Easily the best source of it so far reported is *Eucalyptus macrorhyncha*, the leaves of which contain 7-8%.

It is gratifying to note that the Council for Scientific and Industrial Research has appointed special officers to study the alkaloids in Australian plants, and that with their cooperation and, no doubt, stimulated by Dr. Briggs's lectures, some of the organic chemists at the University of Sydney have established a vigorous school of alkaloid research there. The stated aim of our Society emphasises our interest in the study of natural products, and may I say that soon again we hope to see renewed at the Technological Museum the work on essential oils that has been so badly interrupted by the war. There are some chemists in Australia who are of the opinion that work on natural products is out of date and unimportant when compared with what they are pleased to call "tailor-made molecules". It is quite a sobering experience to compare the efficiency of most tailor-made bacteriostatic drugs with that of the natural product penicillin; and it will be a sad day for science when Nature can present no more intriguing puzzles for scientists to unravel, or useful lessons for them to learn, for the elucidation of the complexities of natural phenomena has not just contributed to the enrichment of our sciences but has been their very flesh and blood and bone.

When we recall again the aim of our Society to develop the natural resources of Australia, we are particularly glad to congratulate the Minister of Education, Mr. Heffron, for his vision in establishing an Institute of Science and Technology in Sydney offering degree courses of study in science and engineering; and his wisdom in decreeing that the results of all research carried out in the Institute will be freely available to all. The scientific work of the United States of America has been greatly enriched in the past by the researches carried out in such famous institutes of technology as M.I.T. and Caltech.

During 1946 the Australian and New Zealand Association for the Advancement of Science resumed its nation-wide scientific conferences with a highly successful meeting at Adelaide. We rejoice at this evidence of the return of pre-war conditions, and extend our good wishes for the success of the A.A.N.Z.A.A.S. meeting at Perth this year.

It is gratifying to record that the finances of the Society remain in a healthy state. Once again the Government of New South Wales made a grant of £400, and this has been all the more welcome because of rising costs in the printing industry.

The number of books and parts of periodicals received by the library this year has noticeably increased, partly because of the receipt of back numbers delayed over the war period, partly because of extended changes. As a result of continued new accessions space in the library is becoming limited, and it will not be many years before a serious problem may arise. During the year a conference was arranged between representatives of the different owner bodies to consider the possibility of combining all three libraries in Science House into one when the extensions are undertaken in the future. However, unanimity on the proposal for unity put forward by the Royal Society was not attained. Mr. H. W. Wood has continued to act as Honorary Librarian during this year, and the thanks of the Society are due to him for his devotion to the best interests of the library.

Dr. Edgar Booth, a past President of this Society, of the Wool Secretariat, and Mr. Alan Maccoll, worthily represented the Society at commemoration celebrations in honour of Sir Isaac Newton held in London last July.

I should be ungrateful if I were not to express my appreciation for all the assistance and kindnesses I have received from the officers and Council of the Society during my year of office. At all times there has been willing assistance. Particularly, I should like to thank the Honorary Secretaries, Dr. D. P. Mellor and Mr. F. R. Morrison, and very especially Dr. Adolph Bolliger, on whom I leaned heavily for advice, and who took over the duties of the presidential office whilst I was abroad.

It is with regret that I announce the loss the Society has sustained through death, during the year, of three members.

HENRY GORDON FARNSWORTH (1877-1946) was a member of our Society since 1921. He joined the Public Works Department of this State when a young man, and rose to be Chief Inspector of the Stores Branch. He was particularly interested in lubricating oils and had built up a private laboratory for their testing. He was a noted horticulturist, being very fond of roses, and often planned gardens for his friends.

SIR GEORGE JULIUS, who died in June, 1946, joined the Royal Society of New South Wales in 1911. He was a graduate in Science and Engineering and won a high place in the scientific life of Australia. He played an important part in the founding and progressive development of the Institution of Engineers of Australia and the Standards Association. He will be chiefly remembered, however, for his work in connection with the Council for Scientific and Industrial Research, from the presidency of which he retired at the end of 1945. The achievements of the officers of the C.S.I.R. over the last twenty years are a tribute to his initiative, organising ability and forceful leadership. He played a big part in the Australian National Research Council and was a leader in the Rotary Movement. Probably he will be best remembered as the inventor of the totalisator, that practical calculating machine which was in some ways a forerunner of the amazing electronic calculating machines of today. He was also noted for his hobby—the building and operation of model railroads.

CARL ADOLF SUSSMILCH, was distinguished by his long and loyal service to the Royal Society. As a young man he became interested in geology and mining. Later he entered the service of the New South Wales Department of Education and was successively Lecturer-in-charge of the classes in Mining and Geology at Sydney Technical College, Principal of Newcastle Technical College, Assistant Superintendent of Technical Education, and before retiring, Acting Superintendent.

He was President of this Society in 1922, and served on the Council and in executive positions for many years. He was also President of the Linnean Society and Section C of the A.A.N.Z.A.A.S. Mr. Sussmilch was a great humanitarian, and did yeoman service for the Society of Crippled Children.

As a scientist he was chiefly known for his contributions to geomorphology and palæozoic stratigraphy. His book, "The Geology of New South Wales" was long a standard introduction to New South Wales stratigraphy and physiography.

PART II. FREEDOM OF SCIENCE.

Professor Elkin, in his Presidential Address to this Society in 1941, discussed the difficulty which confronts the retiring President, who, by tradition, is charged with the duty of preparing and delivering a Presidential Address to a quorum of the members. Traditionally, also, the first part of the address is a brief survey of the life of the Society and its interrelationships with the community during the preceding year. The choice of the subject matter of the second part of the address, however, has always been left to the personal decision of the retiring President. Usually, but not always, the form of this latter half has been that

of a review of the results of the President's own personal researches, combined with a survey of the special field containing those researches. Let me say here and now that I should have fallen into line with this conception of the requirements of the second half of the Presidential Address had it not been for an entirely unexpected happening during the year.

The American Philosophical Society, "held at Philadelphia for promoting useful knowledge", and the National Academy of Sciences of America, at Washington, D.C., decided last year to invite delegates from sister academies of science throughout the world to attend their autumn meetings in October of 1946, generously offering to defray all the expenses connected with the visits. I received a letter from Dr. Gates, President of the American Philosophical Society, and Dr. Jewett, President of the National Academy of Sciences, inviting me to nominate a representative of the Royal Society of New South Wales to attend the conferences. When the matter was put before the Council it was agreed that I, as President, should be the one to go to America.

In due course I travelled by air to Philadelphia and was there in time for the opening sessions of the American Philosophical Society's meeting. The meetings of the National Academy of Sciences followed, and at their conclusion I became one of a party of the visiting delegates who made a nation-wide inspection of important research centres in the United States of America.

The foreign delegates to Philadelphia and Washington came from many countries—from Australia, Belgium, Brazil, Canada, China, Czechoslovakia, Denmark, England, Finland, France, Greece, Holland, India, Italy, New Zealand, Norway, Peru, Roumania, Russia, Sweden and Switzerland. They had magnificent opportunities for getting to know one another, and the distinguished American scientists who acted as their hosts. Very many new personal friendships were formed as the result of the visits, and it is fair to say that the friendly meetings and personal exchange of ideas between scientists was at least as valuable a factor towards the reconstruction of some portion of the international community of science as were the important discussions which dealt with the formal machinery of international scientific cooperation, such as the International Scientific Unions and U.N.E.S.C.O.

Nevertheless, even to an Australian, from a land remote from the great centres of life and civilisation, where the inhabitants are inclined to regard the course of events in other lands with aloofness or frank disinterestedness, it was obvious that despite the intense longing and the utmost willingness of scientists from all parts of the world to return to the days when it could fairly be claimed that science belonged to all the world and had no national frontiers, and when scientists from all countries could meet simply as scientists and freely interchange ideas and friendly criticisms in a common search for truth, there was a conviction that such a return was not yet in prospect.

There was a general recognition that freedom of science, as we have known it, is in serious danger of being permanently disfavoured by the vast majority of the non-scientific community, and that the regimentation of scientists and the unrestricted use of the discoveries of science in time of war, seen now clearly for what they are—perversion of science—have brought mankind to the very brink of an abyss.

The dropping of atomic bombs on Hiroshima and Nagasaki, and the subsequent Bikini atoll tests have convinced all thinking persons that another great war would mean the end of civilisation as we know it. Let there be no doubt of that. Last week you heard what His Excellency Lieutenant-General Northcott had to say of Hiroshima and Nagasaki after personally inspecting what little remains of those once flourishing cities. That there is no defence against atomic bombs is attested by the most distinguished physical scientists who have had anything to do with their development. In America there is a

special committee headed by men like Einstein, Urey and Morse, charged with the duty of convincing all Americans that war in this atomic age is equivalent to national suicide.

Is there any wonder that, faced with such a prospect, unable to understand how it has been brought about, except that somehow or other scientists and science are heavily involved, the common man cries, "Enough of science!" That is the position the scientist of today faces. If he is to be allowed freely to carry on with his experiments and studies and freely to communicate his results to all the peoples of the world as before, then the non-scientific world has the right to demand that it be convinced that such freedom will not hasten a final disaster.

Before the falling of the first atom bombs there were many who were only too conscious of how destructively perversion of science was effecting human relationships. Hiroshima and Nagasaki brought it into sharp focus for all. Is it any wonder, then, that at Philadelphia and Washington there were still many doubts and forebodings and a feeling of frustration? Sir Henry Dale, who delivered the Pilgrim Trust lecture at Philadelphia, crystallised into words the vague perceptions of the many by discussing this very question of the Freedom of Science, and I should fail in my duty as your delegate to America were I not to bring to your notice some of the views he there expressed, or to do all I could to help to re-establish that international cooperation we once knew as the international community of science.

The physical scientist who looks back over the vast panorama of human history may be forgiven if he views it from a standpoint other than the traditional and sees the gradual progress of man in the control of his material environment as a step-by-step mastery over the sources of energy in Nature and their subjugation to the needs of life, rather than as a successive mastery over the materials employed for the making of weapons, such as the ages of stone, bronze, and iron. He can take some comfort from the realisation that mastery of the energy of fire has been applied, in the long run, to creative and beneficent ends, and that there has been a gradual evolution of civilisation from savagery. The progress has certainly not always been forward. There have been many setbacks, and the energy of fire has been frequently used to destroy much of man's achievements through the ages. This was vividly brought home to us by the great bombing raids of the war just ended. Man, in his mastery of the energy of fire, has always had the choice—whether to use it for the purposes of life, or for destruction.

Until the dropping of the first atomic bomb on Japan, the most significant event in the history of human progress occurred in the year 1774, when James Watt perfected the steam engine and showed how the energy of fire could be used to free man from the drudgery of animal labour. The scale on which man could live could then be pushed up according to the scale on which he could draw on the energy of fire to perform his mechanical tasks. Even with the steam engine, however, it would not have been a very much bigger scale had man remained dependent on the timber of the forests for fuel. It was the simultaneous tapping of the vast capital stores of fossil fuel, coal, locked up in the earth's crust back in the Permian and Carboniferous era, which enabled him to develop the invention of the steam engine so as to get ever-increasing amounts of mechanical energy for the purposes of life. For the first time in his history man possessed the power to push up his scale of living to any desired extent; and the scale on which a modern material civilisation can develop is dependent on the extent to which supplies of fossil fuel energy are available to it.

The great wars we have witnessed in these last thirty years have been, in the main, struggles for control of the sources of energy—as evidenced, for example, by the great German drive towards the Caucasian oilfields that was

stopped at Stalingrad. It is significant, too, that even at the present time much of the world unrest, as in Palestine and the East Indies, is in countries strategically located near great oilfields.

The earlier discoveries of physicists in their studies of radioactivity made it possible for them to visualise the possibility of artificial transmutation of elements, with the release of quantities of energy—atomic energy—of the order of a million times greater than what is obtainable from ordinary chemical reactions, such as the combustion of coal. Many of these earlier scientists also clearly foresaw, after the misuse of science in the 1914–18 war, that discovery of the means of unlocking supplies of atomic energy would be at once followed by attempts to prepare a super-bomb for the purposes of destruction. At least one of them, Frederick Soddy, of Oxford, who had won a Nobel prize for his researches into the phenomena of radioactivity, became so concerned with the appalling prospects of what would happen to a world whose people could not agree how to divide the abundant benefits available from the utilisation of enormous supplies of fossil fuel when atomic energy was tapped, that he deserted physical science and set out on a forlorn quest to convince a heedless mankind of the dangers with which it would one day be faced—"laying himself open", to use his own words, "to the abuse which passes for argument in matters that affect the pocket rather than the mind or soul".

Soddy had about as much success as Noah, and it is fair to say that his scientific colleagues resented his incursion into economics as much as did the economists. It is interesting now to read the prophetic words he wrote over twenty years ago about the discovery of the means of obtaining atomic energy. "If the discovery were made tomorrow there is not a nation that would not throw itself heart and soul into the task of applying it to war."

The magnitude of the tragedy for science that this, the most important scientific discovery ever made, with its triumphant verification of scientific prediction and all its promise for the expansion of human life and happiness, should have been made in time of war under the cloak of war secrecy, and used, not for the exaltation of life, but for its destruction, cannot be overestimated. The stupendous realisation that not merely in the remote stars, like the sun from which all our energy has been previously drawn, but at our very feet are stores of energy a million times greater than any we have yet known, has, as yet, passed the common man by. He can only look at the event not as the presentation to him of a choice between the use of atomic fire for the purposes of life or for destruction, but as nothing but a threat to his very existence. There is no wonder that for him atomic energy is synonymous with annihilation, nor that he should seek to prevent any race to produce bigger and better atomic bombs, and the free exchange of the results of nuclear chemists and physicists which could, in his opinion, lead to it.

To the scientists, however, the real shock was the clear recognition of just how far the misuse of the greatest gifts of science had taken man along the road to complete disaster. What had started with the introduction of poison gas into warfare in 1915 had led to a perversion of the real purposes of science so complete that even yet, with hostilities long past, military secrecy still demands silence on some of the greatest discoveries of science.

The scientist, who, in defence of his free science, and his very all, willingly endured the secrecy imposed on him by war is now vitally concerned lest science become permanently enmeshed in a web of secrecy. Against such a disaster we have the right as scientists to tell the citizens of the world of which we too are citizens, that secrecy and science are as the poles apart; that secrecy poisons the very spirit of science; that the real purpose of science is the bringing of Nature's secrets into the light of day; and that failure to free science in times of peace from the secrecy it accepted as a necessity of war will lead inevitably to

the blotting-out of all the fair prospect of a civilisation beside which "the triumphs of our times would appear tawdry, and our struggles for energy as a horrid dream".

If we claim that right, however, let us remember that inevitably we shall be called upon to justify it. We shall be told, and are being told, that free disclosure of all the results of science, without thought of the uses to which the advancement of natural knowledge is to be put, would jeopardise national security. To that we must answer that the brotherhood of science is international, not national; that science is for all humanity, not for single nations; and that the fruits of science are for life and living, not for destruction. The history of Germany in the last fifteen years has shown only too clearly how the enslavement of science in secret preparation for the destruction of other peoples leads inevitably to its own destruction.

Even as a matter of expediency, all military and industrial experience shows that, at best, the advantages secrecy confers are never permanent. At most, it enables nations or industrial concerns to keep only one jump ahead of their rivals. Secrecy begets secrecy and mistrust. It is like the cancer cells which start so much like healthy cells, but, in the end gnaw away the very vitals. I think that we here would agree that it is the secrecy imposed on the people of Europe's greatest nation at the present time that is so largely responsible for the mistrust of other nations. Democracy has had one bitter experience of secret preparation for war; and it is not for us, who are not charged with the tremendous responsibilities of national leadership, to dictate the actions that should be taken to guard against any possible secret preparations. But it is our right to deplore that secrecy, and to announce clearly and unmistakably to the world what we hold passionately to be true—that international brotherhood and peace can only come through the free and willing interchange of human ideas, and that not the least important factor in creating international co-operation and goodwill is the international community of science.

It has been the contention of all the great leaders of science that the pursuit of truth, without thought of the uses to which it may be put, is the first duty of science; but it is equally well recognised that the application of the results of such voyages of pure scientific discovery not only can, but often does, result in immense benefits to humanity, and the benefits are often far greater than those obtained by researches designed by the scientific planners. As Soddy puts it, "In scientific research nothing is less likely than that the discoverer will discover what he sets out to discover." . . . "Pasteur, studying optical isomerism, was led to the study of fermentation in passing on the road to the recognition of the part played by bacteria. But the most important part of his work was neither in brewing nor saccharimetry. It revolutionised surgery and to it countless millions owe their lives." Perkin, setting out to synthesise quinine, prepared the first coal-tar dye, and founded the great colour industry of today.

"Scientific discovery is a growth rather than a journey according to plan. The voyage may be west to discover the east, and it is through fog and dead reckoning to put places upon rather than to hit them off from a map." So clearly recognised is this principle that the most abstruse researches may eventually serve mankind and that the full flowering of scientific genius can only be attained where there is freedom to follow the search, wherever it leads, that even in industrial research organisations, where so much study of specific problems in restricted fields is demanded, the man with vision and inspiration is given his head.

You may ask now what we here should do to help preserve that freedom of science which has been responsible for so many benefits to this country. Let us recognise at the outset that the great nations of the world, with whom rests the disposition of nuclear science, will little note what we say or do here; but

we can play a part, small in itself, but none the less important in the firm re-establishment of the international community of science. Already Australian science has taken its place in the International Scientific Unions and in the United Nations' Educational, Scientific and Cultural Organisation, and it is not irrelevant to note here a report by Professor Noyes, President of the American Chemical Society, on the recent meetings of U.N.E.S.C.O. at Paris, in which he commented, "If all international groups could come to agreement as easily as the scientists, many of the problems of the world would be solved in short order".

Next, we should clearly recognise that freedom of science today demands something more than the free interchange between scientists of the results of scientific research, couched in the jargon of science, which is unintelligible, and therefore secret, to the layman. If we demand freedom for ourselves from the constraints of secrecy, then surely it is our duty to interpret the results we obtain as well as we are able, and as often as is necessary, into the common language of the layman, and so to prevent the charge that we keep our results secret from him.

During the past year we have had five popular science lectures delivered. We could increase the number. We could make more use of the radio and the newspapers. It goes without saying that those of us who lecture in educational institutions should do all in our power to impart to our students the ideals and real purposes of science, but even in these institutions we could do more. Scientists can influence the students of science they teach but they may never even meet those students of the humanities who later become leaders in the non-scientific community. Surely it is our duty to endeavour, with some type of popular interpretation of science, such as might be given in lunch-hour lectures, to develop in them at least some sympathy, understanding and respect for science and its high purposes.

We would do well to begin at once to present to our own people the other side of the picture that the unlocking of the secret of atomic energy presents to mankind—a realm of possibilities beyond the vision of even our most far-seeing scientists. Man's progress in the past has come from his mastery of the sources of energy. Already he has learned much about the mastery of atomic energy. Uranium-graphite piles are already a practical source of heat energy, and atomic energy will soon be adapted for large stationary power plant units. In the future the atomic energy units using practically pure uranium 235 or plutonium will be much more compact. On the material side the gains seem even more imposing at the present time. Nuclear chemistry has led to the synthesis of four new trans-uranium elements, neptunium (93), plutonium (94), americium (95), and curium (96) by transmutation reactions from uranium. Plutonium is at present by far the most important of these, for it can be used to make atomic bombs or atomic power plants according to man's will. At least one radioactive isotope for every element in the series from hydrogen to curium has now been made and radioactive isotopes of most of the important elements can be made in quantities. The possibilities for research in the realms of pure chemistry, biochemistry and biology with labelled "tracer atoms" are unlimited, and already there is a flood of results obtained by their use.

There is another way in which we could endeavour to report the results of science to the non-scientific citizen. We could seek to enlist into the membership of our Society citizens who are not scientists, but who, nevertheless, love truth for truth's sake and would be prepared to come into partnership with us in our Society, as a kind of secular arm. Such an expansion of our membership would be no novelty. In 1935, for example, numerous citizens of good standing, interested in the aims and objects of the Society, were invited to become members, and many accepted the invitation.

It does not need me to emphasise the importance of endeavouring to enlist into our Society all those novitiates in science who will soon become graduates and on whose shoulders some day will rest the scientific hopes of this community. At Philadelphia, Sir Henry Dale recalled that over 200 years ago Benjamin Franklin used to require from every candidate for admission to the earliest of American learned societies an affirmative answer to the question "Do you love truth for truth's sake, and will you endeavour impartially to find and receive it for yourself, and communicate it to others?" If we could imbue our young men with the spirit of that rule we should have little to fear for the future of science in this country, and when the time comes, to pass on to them the torch, with the words of Alfred Noyes—

"Take thou the splendour, carry it out of sight
 Into the great age I must not know,
 Into the great new realm I must not tread."

One of the great difficulties in the instillation of the real spirit of science into young men and women in this country is the lack of graduate schools. It is fair to say that it is at the universities and to a lesser extent, the technical colleges, that the spirit of free enquiry flourishes most vigorously. The longer the time our young men can spend in the atmosphere of such institutions, the greater should be their desire to seek truth for truth's sake. Some of our universities have recognised the deficiency and are now preparing to offer the Ph.D. degree. Two extra years of training and research and maturity should prove of infinite value. There are some difficulties to be met, such as the provision of finances and the dangers of inbreeding, but participation in some university teaching work, and the adoption of the practice obtaining in America, of strongly recommending students to attend a graduate school other than the school from which their first degree was obtained, could greatly strengthen science in Australia.

The value of the interchange of students and mature scholars, not only between Australian universities, but with educational and research institutions all over the world, cannot be over-emphasised. The best way of understanding other peoples and their problems is to live with them; and nothing makes a greater contribution to the international community of science than this friendly interchange of scientists. Lest any should fear that Australia could offer little to attract scientists from abroad on exchange, let me assure them that in America at least, particularly among the young men, I found not only willingness but even eagerness. It is true that Australia cannot offer such magnificent research facilities as some other countries, but a little intelligent scientific planning would greatly help. Let me make one suggestion. Every department of organic chemistry in Australia is more or less compelled to carry a large stock of organic chemicals. Each laboratory probably requires only a little of each of these, so that supplies are purchased in the worst markets. Because of our remoteness from the manufacturing countries it takes months to replenish exhausted stocks. If there were one central Australian store, maintained by the Government, whose purpose was to purchase in quantity at cheap prices and to carry a complete range of every chemical manufactured, many chemical research projects could be smoothly maintained instead of being interrupted, or, as often happens now, completely abandoned.

It is unthinkable that here in time of peace authority should ever demand concealment or distortion of any new scientific discovery. Nevertheless we must be on our guard to prevent it ever from happening. To that end it is of paramount importance that we should maintain and control some instrument of free publication. The members of this Society take pride in the long record of publication of our Journal, which is widely circulated to free scientific institutions

throughout the world. The results it records may not always be great or important, but they stand in their place to be freely used by all who desire. During this year it was suggested to the Council that the decision of the Council of Scientific and Industrial Research to publish an Australian journal of research would dispense with the need for a journal such as ours, and that soon, whether we liked it or not, lack of contributions would force us to cease publication. Nothing could be more catastrophic for free science in this country than such a result. Despite the obvious advantages of rapid publication and perhaps wider circulation, the danger of control of publication by a government department, whose policy can be rapidly altered by whatever political party is in power, are even more obvious. It was reassuring only a few days ago to read of Sir David Rivett's forthright declaration for scientific freedom, but Sir David Rivett will not always be Chairman of the Council for Scientific and Industrial Research.

I have tried to reproduce for you some of the important arguments put forward to us at Philadelphia by Sir Henry Dale, and to study the lessons they have for us here. I cannot do better in concluding them than to quote the actual words with which he closed his lecture there. Here they are :

“ It is not without significance that, whereas history, literature, art, and even religion all have national characters and local attachments, science alone of man's major intellectual interests, has no frontiers and no national varieties ; that science, like peace, is one and indivisible. And science, we should insist, better than any other discipline, can hold up to its students and followers an ideal of patient devotion to the search for objective truth, with vision unclouded by personal or political motive, not tolerating any lapse from precision, or neglect of any anomaly, fearing only prejudice and preconception, accepting Nature's answers humbly and with courage, and giving them to the world with unflinching fidelity. The world cannot afford to lose such a contribution to the moral framework of its civilisation, and science can continue to offer it only if science can remain free.”

THE ORBIT OF h 3494 ($2^h 15^m \cdot 6$, $-35^\circ 54'$: 1900).

By HARLEY W. WOOD, M.Sc.,
Sydney Observatory.

Manuscript received, March 19, 1947. Read (in title only), April 2, 1947.

The motion of this double star was examined in 1931 by Finsen, who gave three sets of elements based on measures up to 1930. Measures since that time have departed more and more from the ephemerides corresponding to these orbits so that a recalculation seemed worthwhile.

The orbit was calculated by the method of Russell (1933) in the following steps:

(a) The observed values of position angle (p) and distance (d) were plotted separately as ordinates on squared paper with time in each case as abscissa. Smoothed curves adjusted to obey the law of areas were drawn among these points.

(b) Values of p and d were read from the graphs of step (a) and plotted as polar coordinates to obtain the Russell parameters of the apparent ellipse. On account of the restricted length of the observed arc a considerable range in the values of these parameters will represent ellipses following the curve to the accuracy expected. However, when an ephemeris is prepared each computed place, by plotting on the curve, can be made to yield a value of the periastron time (T) from the equation $T = M - t$, where t is estimated from the curve. The range of parameters is much reduced by the fact that the various values of T thus obtained should agree.

(c) The Thiele-Innes elements (see for example Aitken, 1935) were then computed and an ephemeris prepared from them for comparison with normal places derived from the curves of step (a). The residuals having been listed in order of the magnitudes of the coefficients in the equations of condition of the correction to one element, this correction was estimated—similarly for the other elements. This is easily done by dividing the list into groups in a way similar to that often used to obtain plate constants in photographic astronomy. A least square solution, frequently not warranted by the percentage accuracy of double star data, is thus avoided.

The normal places and the residuals O-C from the ephemeris of the adopted orbit are shown in Table 1. The third and fifth columns give respectively the residuals in position, angle and distance.

TABLE 1.
Normal Places.

Date.	p	O—C	d	O—C
1855	108°·7	—0°·1	1"·74	—0"·02
1885	80·1	+0·2	1·47	+0·03
1900	56·6	—0·5	1·13	—0·03
1920	5·5	+0·1	0·92	+0·02
1930	335·4	+0·1	0·95	—0·01
1935	322·2	—0·1	1·02	0·00
1945	300·9	—0·1	1·18	+0·01

TABLE 2.
Observations.

Date.	p (1900)	$O-C$	d	$O-C$	Nights.	Aperture.	Observer.
1837.91	122°.8	+0°.1	1°.58 (est)	-0°.19	3	18	h
52.82	110.2	-0.4	1.96	+ .19	2-1	6.2	Jc
77.87	88.3	+0.3	1.54	- .01	2	11	Hwe, Stn.
87.94	75.6	-0.5	1.42	+ .03	1	11.4	Pol
92.97	67.9	-1.1	1.19	- .11	2	11.4	Slr
97.10	65.8	+3.5	1.69	+ .47	3	11.4	Slr
97.72	62.1	+0.9	1.28	+ .08	1	24	See
1899.47	58.0	-0.1	1.07	- .10	3	24	Cog
1905.98	32.2	-12.3	1.20	+ .15	2	26	Ol
09.77	31.8	-3.4	0.93	- .06	2	12	Ol
15.09	18.9	-1.4	0.96	+ .03	4	9	V
17.01	14.0	-0.6	0.92	- .00	2	9	I
19.82	6.4	+0.4	0.88	- .04	4	17	δ
20.94	3.0	+0.5	0.90	- .01	3	17	δ
21.0	2.8	+0.5	0.96	+ .05	2	9	I
22.92	356.2	-0.1	0.94	+ .03	3	17	δ
24.82	351.1	+0.7	0.94	+ .02	4	7.4	V
25.89	350.7	+3.5	0.80	- .12	3	26½	φ
26.65	344.3	-0.7	0.90	- .03	4	7.4	V
28.64	338.2	-1.0	0.95	+ .01	5	7.4	V
28.72	340.3	+1.4	0.90	- .05	4	7.4	tBr
28.82	338.6	-0.1	1.02	+ .07	1	17	δ
28.87	333.7	-4.8	1.05	+ .10	4	9	B
29.95	334.9	-0.6	0.92	- .04	4	26½	B
30.02	335.5	+0.3	1.08	+ .12	4	15	Wlq
30.69	333.4	-0.1	0.92	- .05	5	24	V
31.80	329.4	-1.1	0.92	- .06	4	26½	B
31.96	329.3	-0.7	0.92	- .06	4	26½	φ
32.59	328.0	-0.4	0.90	- .09	4	24	V
32.60	325.8	-2.6	1.02	+ .03	3	17	δ
33.90	324.8	-0.2	0.96	- .05	4	26½	B
34.61	323.2	-0.1	1.02	- .00	8	26½	φ
34.63	324.3	+1.1	1.04	+ .02	3	17	δ
34.96	321.4	-1.0	0.97	- .05	4	26½	B
35.62	320.5	-0.4	1.08	+ .05	4	24	V
36.93	317.9	+0.2	1.04	- .01	2	26½	φ
37.12	316.9	-0.4	0.99	- .07	4	15	Smm
38.13	315.9	+0.9	1.03	- .04	4	26½	B
38.67	314.1	+0.3	1.05	- .03	3	24	V
38.97	314.0	+0.9	1.11	+ .03	1	26½	φ
42.63	305.4	-0.1	1.16	+ .02	4	15	V
44.67	301.3	-0.3	1.12	- .05	4	24	V
44.74	302.4	+1.0	1.10	- .07	4	26½	B
46.69	296.7	-1.2	1.36	+ .17	8	11.4	Wood
1946.92	297.5	0.0	1.25	+ .05	4	9	Stromlo

Table 2 gives the observations and comparison with computed places. Columns 1 to 5 are as for Table 1, and the remaining ones give the number of nights, the aperture of the telescope in inches, and the observer. I am much indebted to Dr. W. H. van den Bos for sending me a copy of measures from his card catalogue at the Union Observatory, Johannesburg, and to Dr. J. G. Voûte for measures made at the Bosscha Observatory, Lembang, and to Dr. R. v. d. R. Woolley for the Stromlo measure. So far as they were available to me, the original publications were examined and in the case of Sydney measures the original observation books. The only points worthy of remark are that the 1877.87 measure has been given the weight of two nights since although the measures were made on one night it is the mean of two by different observers

and for 1892·97 one Sydney measure, made on a night noted as very poor, has been rejected.

The elements, still based on a somewhat inadequate arc, are as follows:

P .. 250 years,	Ω .. $100^{\circ} \cdot 7$,	A .. $+1'' \cdot 119$,
n .. $-1^{\circ} \cdot 439$,	ω .. $122^{\circ} \cdot 4$,	B .. $-0'' \cdot 646$,
T .. 1931·95,	i .. $137^{\circ} \cdot 5$,	F .. $-0'' \cdot 364$,
e .. $0 \cdot 24$,		G .. $-1'' \cdot 420$,
a .. $1'' \cdot 57$		

and the corresponding ephemeris:

Date.			p	d	Date.			p	d
1945	301°·0	1″·17	1970	263°·1	1″·38
1950	292·2	1·24	1975	256·4	1·38
1955	284·3	1·29	1980	249·7	1·38
1960	276·9	1·33	1985	243·0	1·37
1965	269·9	1·36	1990	236·2	1·36

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DIMENSIONAL METHODS IN THE DESIGN OF INDUSTRIAL CHEMICAL RESEARCH.

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THE NATURE OF INDUSTRIAL CHEMICAL RESEARCH.

The number of commercial firms engaged in manufacture, and in particular in chemical manufacture, which support what are referred to as research departments has increased all over the world in the last two decades and now constitute an appreciable proportion of the total scientific effort of any particular country. The question may well be asked as to what is the nature of the work done by such departments. I think it is fair to claim that much of the so-called industrial research might better be termed developmental work or the practice of adapting known physical and chemical principles to the attainment of economic ends. There is a great difference between showing that a certain desirable chemical product can be produced in the laboratory as a result of a certain chemical reaction and the design of a plant to carry out that reaction on a factory scale. Whether the discovery of the original reaction or the design of the final plant is the more laudatory achievement is a point on which the industrialist and the pure scientist will never agree; but whereas basic physico-chemical theory provides a guide to the attainment of new discoveries, there is no corresponding theory for the design of developmental research. The method adopted is almost entirely one of trial and error.

The "industrial research chemist" repeats the original experiment in terms of the description in the chemical literature and checks the experimental working conditions for optimum yield. He then repeats the experiment on a slightly larger (the so-called sub-pilot) scale and redetermines all the experimental parameters. Usually they are all found to be slightly different from those of the experiment on the laboratory scale. From the results of the sub-pilot scale plant he designs a larger or pilot scale plant and redetermines his working conditions. From these factors he may design the larger or factory scale plant.

At each change in scale there is, usually, an apparent change in the optimum working conditions often not attributable to any error in the experiments on the smaller scale. That there is such a progressive change in the optimum working conditions is simply accepted and practically no attempt has been made to explain why such a change should occur or whether there is a more efficient way of designing factory scale plant from reaction characteristics. One of the objects of this paper is to inquire how we should go about looking for such a more efficient method.

THE POSITION WITH REGARD TO OTHER SCIENCES.

The problem of designing effective large scale equipment from the performance of small equipment is by no means a problem peculiar to industrial chemistry, but is one which has been faced in many branches of applied science such as hydraulics, aerodynamics, ship building, structural engineering and more recently in the design of heat transfer equipment. In each case the problem is one of the dimensions of the variables concerned.

Consider a full scale bridge and a model at, say, one-tenth scale, geometrically similar and constructed from the same material. Consider any particular member of the model. Its volume, and therefore its weight, is one-thousandth that of the full scale or prototype, while its strength, depending on the cross-sectional area, is only one-hundredth that of the prototype. To make the model and prototype dynamically similar, or similar with respect to the balance of forces, it would be necessary either to make the model from denser material or material of lower yield stress. If the two bridges are dynamically similar, then the ratio

$$\frac{\text{Yield stress}}{\text{Density} \times \text{Acceleration due to gravity} \times \text{Linear scale}}$$

must be the same in both. This factor, as the reader may readily verify for himself, is one of zero physical dimensions.

The flow of fluids in two different sized vessels exhibits dynamical similarity when the quantity

$$\frac{\text{Velocity} \times \text{Linear dimension} \times \text{Density}}{\text{Viscosity}}$$

is the same in both vessels. This is also a quantity of zero dimensions and has been given the name Reynolds number.

Many similar examples could be given, and we may take it as a rule that the condition of dynamical similarity between two systems on different scales is determined by the equality of certain dimensionless quantities describing the state of the systems; and that only when the state of a system is described by equation between dimensionless quantities is it expressed in a form independent of its geometrical size.

The various quantities used to describe the state of a physico-chemical system include: flow rate, temperature, rate constant, equilibrium constant, pressure, space velocity, space time yield. None of these quantities is dimensionless. Indeed rate and equilibrium constants are properties so badly defined that they have different physical dimensions for each different order of chemical reaction. In consequence, therefore, when the industrial chemist expresses the results of an investigation into the possibilities of a certain reaction in the form of a functional relationship between, say, temperature, space velocity and space-time yield, he, by the use of non-dimensionless quantities, obtains empirical expressions which involve dimensional constants, themselves a function of undetermined variables including the geometrical scale of the equipment used. Accordingly the empirical "constants" may be expected to be different in each different sized apparatus. One of the first tasks of dimensional methods in industrial chemistry is to express the results of an investigation in such a form that the results are equally applicable to small or large scale equipment. This we can do if we find the means for setting up a condition of chemical similarity between reactions in different sized vessels.

ATTEMPTS TO SET UP THE CONDITIONS FOR CHEMICAL SIMILARITY.

A theoretical basis for a theory of chemical similarity was given in 1936 by G. Damköhler (1936). He took as fundamental axioms the conservation of mass, energy and momentum and wrote down these expressions in vector form for an elementary volume in a chemical system. He then took as his dimensionless parameters the ratios of all pairs of terms in the resultant set of equations (this is standard practice) and obtained five such quantities. He claimed that two chemical systems on different scales would be chemically similar if these five dimensionless quantities each have the same value in the two scales. Damköhler found that simultaneous satisfaction of these five conditions was only possible in a few special instances.

Edgeworth Johnston (1939) has discussed this work of Damköhler and has pointed out that in his general equations Damköhler has too many variables; he has ignored the necessary relationship between reaction rate and temperature and also he has not taken into account the fact that the boundary conditions for the energy equation can be adjusted independently of the scale by means of lagging or adiabatic jackets.

Laupichler (1938) has attacked the problem in a somewhat different manner. Working on the water gas exchange reaction, he obtained an expression for the overall chemical driving force and for the overall rate. The quotient of these two he calls the chemical resistance. This resistance he splits into two parts in series; a transfer resistance and a thermal resistance. The value of each of these resistances can then be evaluated in terms of the physical properties of the system. The performance of a large scale system can then be calculated from the resistance terms. The method of Laupichler has been extended by Hurt (1944).

THE VARIABLES CONCERNED.

In presenting the physical problem exhibited by a change of scale of a chemical system we shall proceed on a generalized method based on the treatment of Damköhler. The first step is to decide what variables are necessary in order to specify the system. We shall consider first a homogeneous system involving m different molecular species. From the phase rule we know that $m+1$ variables are necessary in order to fix the state of such a system. The following quantities will therefore fix the state of the system:

- (a) The concentration of the molecular species ($m-1$ variables).
- (b) The energy or the entropy (1 variable); and
- (c) The pressure (1 variable).

Let the atomic species in the system be denoted by A_1, A_2, \dots, A_a , a in number. Let n_{ij} represent the number of atoms of type i in molecules of type j , i.e. the molecule B_j may be represented as

$$B_j = n_{1j}A_1 n_{2j}A_2 \dots$$

Let v_j molecules of type j enter the chemical reaction, which thus may be represented by:

$$\sum v_j B_j = 0$$

or

$$\sum v_j (\prod_i n_{ij} A_i) = 0 \dots \dots \dots (1)$$

Let C_j be the number of grammolecules of type j in unit volume.

If any small element of volume is taken in a continuous reactor, values may be assigned to the controlling properties in that element at any instant. The values will, however, in general change as the element proceeds along the stream. The various factors which produce this change include:

- (a) Change due to chemical reaction, changing the molecular concentration, the energy, the volume, and therefore the linear velocity.
- (b) Changes produced by the stream.
- (c) Changes produced by diffusion across the stream.
- (d) Changes produced by long-hop processes such as low pressure effusion or thermal radiation, or transfer of momentum by sound waves.

Let:

k be the velocity of the reaction in gramme equivalents per unit volume per unit time.

v be the stream velocity in units of length per unit time.

D_j be the diffusion coefficient for the j th component in units of length squared per unit time.

The equation for the conservation of mass then takes the form :

$$\frac{\partial C_j}{\partial t} = -v_j k - \text{div}(\mathbf{v}C_j) + \text{div}(D_j \text{ grad } C_j) \dots\dots\dots (2)$$

where there is no transport by a long-hop process. There are m equations of this type. In these equations $\frac{\partial C_j}{\partial t}$ represents the rate of change in the concentration of component j at some fixed point in the reactor, $v_j k$ represents the rate of destruction of component j per unit volume as a result of chemical reaction, $\text{div}(\mathbf{v}C_j)$ represents the net rate of increase in the concentration as the result of more component j streaming into unit volume surrounding the point under consideration than that streaming out, while $\text{div}(D_j \text{ grad } C_j)$ represents the rate of accumulation at the point consequent upon diffusion of j . The operation div and grad both represent vector differentiations with respect to the distance, div operating on vector quantities represented by clarendon type and grad on scalar represented by italics. Consequently we can write

$$\text{div}(\mathbf{v}C_j) = \mathbf{v}(\text{grad } C_j) + C_j(\text{div } \mathbf{v}).$$

The divergence of \mathbf{v} or the rate at which the velocity changes as a combined result of streaming and the chemical reaction is related to the volume change (ΔV) (in units of volume per gramme equivalent reacting) by the expression

$$\text{div } \mathbf{v} = k \Delta V.$$

Under steady state conditions $\frac{\partial C_j}{\partial t}$ in equation (2) is zero and we have

$$0 = -v_j k - \mathbf{v} \text{ grad } C_j - C_j k \Delta V + \text{div}(D_j \text{ grad } C_j) \dots\dots\dots (3)$$

On combining these physical equations with the one for the chemical reaction we get in all $m+1$ equations in $3m+ma+3$ variables equivalent to one equation in $2m+ma+3$ variables and involving $2m+ma+1$ terms. If every term is to have the same dimensions, then it follows that the ratio of any pair of terms is an expression with zero dimensions. There are $2m+ma$ such independent ratios, and therefore $2m+ma$ independent equations in the $2m+ma+3$ variables. The dimensions of three independent variables may therefore be chosen independently. The independent variables may be most conveniently taken as those of mass (m), length (L) and time (t). The dimensions of the variables in equation (3) therefore are :

v_j	..	0
k	..	$mL^{-3}t^{-1}$
\mathbf{v}	..	Lt^{-1}
div and grad both		L^{-1}
C_j	..	mL^{-3}
ΔV	..	$m^{-1}L^3$
and D_j	..	L^2t^{-1} .

So that every term in equation (2) has dimensions $mL^{-3}t^{-1}$.

Pressure is a measure of the rate of change of momentum across a surface. Thus if we specify the momentum flow across the surface we have fixed the pressure. For the equation of conservation of momentum of our system we may write

$$\frac{\rho \partial \mathbf{v}}{\partial t} = -\rho(\mathbf{v} \cdot \nabla)\mathbf{v} - \text{grad } p + \rho \mathbf{v} k \Delta V + \nu \rho (\nabla^2 \mathbf{v} + \frac{1}{3} \text{ grad div } \mathbf{v}) \dots\dots\dots (4)$$

Where

ρ is the density of the stream,
 p is the pressure, and
 ν is the kinematic viscosity.

In equation (4) $\rho \frac{\partial \mathbf{v}}{\partial t}$ represents the total rate of momentum change per unit volume at a fixed point in the reactor and the various terms on the right-hand side represent the forces acting per unit volume; $\rho(\mathbf{v} \cdot \nabla) \mathbf{v}$ as a result of the excess of momentum carried per unit time into, over that carried out of unit volume by the stream, $\text{grad } p$ as a result of external forces, $\rho \mathbf{v} k \Delta V$ as a consequence of the volumetric expansion produced by the chemical reaction, $\nu \rho \nabla^2 \mathbf{v}$, as a result of the friction forces produced by (ordinary) viscosity and $\frac{1}{3} \nu \rho \text{grad div } \mathbf{v}$ as a result of frictional forces produced by the viscosity of compression. (Brillouin, 1907.) Under steady state conditions $\frac{\partial \mathbf{v}}{\partial t} = 0$, and we write

$$0 = -(\mathbf{v} \cdot \nabla) \mathbf{v} - \frac{1}{\rho} \text{grad } p + \mathbf{v} k \Delta V + \nu (\nabla^2 \mathbf{v} + \frac{1}{3} \text{grad div } \mathbf{v}) \quad (5)$$

There is only one equation (5) having six variables and four terms. There are therefore three independent dimensions which again may be taken as m , L and t . We have, then, for the dimensions of ρ , p and ν

$$\rho \text{ mL}^{-3}$$

$$p \text{ mL}^{-1} t^{-2}$$

$$\text{and } \nu \text{ L}^2 t^{-1}.$$

So that every term in equation (4) has dimensions $\text{mL}^{-2} t^{-2}$.

For the equation of conservation of energy we have:

$$\frac{\partial}{\partial t}(c_p \rho \theta) = -\text{div}(c_p \rho \theta \mathbf{v}) + Qk + J \nu \text{grad } p + \lambda \nabla^2 \theta + \frac{4\alpha}{i} \sigma T^3 \theta \quad (6)$$

where:

Q is the heat evolved by the reaction in units of energy per gramme equivalent. For an isopiestic system $Q = -\Delta H$.

c_p is the specific heat of the reaction mixture at constant pressure.

λ is the thermal conductivity of the reaction mixture.

ρ is its density.

T is absolute temperature of the walls of the reaction vessel, assumed uniform.

θ is the temperature of the point under consideration in excess of wall temperature.

α is the relative emissivity of the reaction mixture.

σ is the Stefan-Boltzmann constant.

i is the ratio of the volume to the surface area of the reaction vessel, and

J is Joule's equivalent.

In equation (6) $\frac{\partial}{\partial t}(c_p \rho \theta)$ is the change in thermal energy per unit volume at any point in the reactor, $\text{div}(c_p \rho \theta \mathbf{v})$ is the excess thermal energy carried into unit volume by the stream, Qk the heat generated per unit volume by the stream, $J \nu \text{grad } p$ is the heat generated per unit volume by friction, $\lambda \nabla^2 \theta$ is the heat transferred per unit volume by thermal conductivity, and $\frac{4\alpha}{i} \sigma T^3 \theta$ is the heat transferred per unit volume by radiation, all measured per unit time. The last term is accurate only under conditions for which the vessel of reaction mixture does not absorb the thermal radiation too strongly and all portions of the vessel are effectively exposed to wall radiation of the same intensity. The internal walls are effectively black, so that the radiation emitted per unit area per unit

time is σT^4 . Of this a fraction α is absorbed by the gas, so that the amount of wall radiation absorbed by any unit volume of gas in unit time is equal to

$$\alpha\sigma T^4 \frac{\text{Area of walls}}{\text{Volume of reactor}}.$$

The ratio Volume/Area we have written as i . For any form of cylindrical reactor i is also the ratio Surface area/Perimeter and may thus be referred to as the hydraulic radius of the reactor (for a circular cylinder i is half the radius). The amount of thermal radiation per unit time sent by unit volume of gas to the walls is clearly

$$\frac{\alpha}{i}\sigma(T+\theta)^4,$$

where θ is the excess temperature of the point under consideration. As long as θ/T may be regarded as a small quantity the net heat loss per unit area per unit time due to radiation is clearly

$$\frac{4\alpha}{i}\sigma T^3\theta.$$

Under steady state conditions the left-hand side of equation (6) vanishes and the equation for conservation of energy may be written

$$0 = -C_p \rho v \cdot \text{grad } \theta - c_p \theta k \text{ div } v + Qk + Jv \cdot \text{grad } p + \lambda \nabla^2 \theta + \frac{4\alpha}{i}\sigma T^3\theta \quad (7)$$

There is only one equation (7) with six terms and nine dimensional variables. Consequently there are four independent dimensions which may be taken as m , L , t and θ (the temperature). In terms of these the dimensions of the variables are :

c_p	$L^2 t^{-2} \theta^{-1}$
θ and T	θ
Q	$L^2 t^{-2}$
J and α	O
λ	$m L t^{-3} \theta^{-1}$
σ	$m t^{-3} \theta^{-4}$ and
i	L .

So that every term in equation (6) is of dimensions $m L^{-1} t^{-3}$.

From the ratio of pairs of terms in equations (3), equation (5) and equation (7) we may derive, after the method of Damköhler, all the dimensionless parameters concerned in the statement of the complete similarity of two different chemical systems. We may, without serious loss of industrial generality, restrict our studies at this point to long circular cylindrical reactors of radius R and length l .

From the mass equation we may derive three dimensionless ratios, viz. :

$$\frac{v_1 k}{v \text{ div } C_1} \quad \text{or} \quad \frac{v_1 k l}{v C_1} \quad \dots \dots \dots \text{I}$$

$\text{div } C_1$ being taken as dimensionally equivalent to C_1/l .

$$\frac{v_1 k}{D_1 \nabla^2 C_1} \quad \text{or} \quad \frac{v_1 k R^2}{D_1 C_1} \quad \dots \dots \dots \text{II}$$

and

$$\frac{v \text{ div } C_1}{C_1 k \Delta V} \quad \text{or} \quad \frac{v}{k l \Delta V} \quad \dots \dots \dots \text{III}$$

In the momentum and energy equations we shall ignore the terms in $\text{grad } p$, which in all usual chemical systems will be small. From the momentum equation

we obtain two dimensionless expressions, one of which is identical with I above. The other is the well-known Reynolds number,

$$\frac{v \text{ grad } v}{v(\Delta^2 v + \frac{1}{2} \text{ grad div } v)} \quad \text{or} \quad \frac{vR}{v} \dots\dots\dots \text{IV}$$

From the energy equation three dimensionless ratios are obtained, one of which is the well known Peclet number, viz.:

$$\frac{\text{div}(\theta c_p \rho v)}{\lambda \text{ div grad } \theta} \quad \text{or} \quad \frac{c_p \rho v R}{\lambda} \dots\dots\dots \text{V}$$

The other two constitute the condition for thermodynamical similarity,

$$\frac{Qk}{\lambda \nabla^2 \theta} \quad \text{or} \quad \frac{QkR^2}{\lambda \theta} \dots\dots\dots \text{VI}$$

and the condition for radiative similarity, viz.:

$$\frac{Qk}{\theta(8\alpha R^{-1} \sigma T^3 - c_p \rho k \Delta V)} \dots\dots\dots \text{VII}$$

in which i has been taken as $\frac{1}{2}R$.

These seven dimensionless quantities are capable of giving a description of any homogeneous chemical system which is independent of the scale of the vessel in which the reaction is carried out. In many cases only some of these quantities need be considered. Thus unless the reaction mixture is very opaque and also the temperature is excessively high the condition for radiative similarity may be neglected and VII becomes equivalent to III, V and VII. If in addition the reaction is approximately isometric, condition III may be ignored. Further if the flow in the reactor is laminar, condition IV may probably be neglected. If the flow is turbulent, both D_i and λ are functions of v .

THE CONDITIONS FOR SIMILARITY IN MODEL AND PROTOTYPE.

If a condition of similarity between a chemical system in a model vessel and one in a large scale or prototype is to be attained, then all seven dimensionless ratios I to VI must have the same value in both vessels. We will consider the case in which the same reaction is studied in both vessels. In doing this we do not exclude the possibility of attaining similarity between two different chemical reactions or between a chemical and a physical reaction such as would be implied by the setting up of the equivalent electrical circuits. We chose the same reaction mixture as the easiest way of attaining similarity with respect to all alternative chemical reactions.

We now have in conditions I to VI equality of the factors v_i , C_i , D_i , ΔV , v , ρ , c_p , Q , λ , α , σ , on the two scales. Conditions of similarity then become

$$\text{I and III} \dots \frac{kl}{v} = \text{Const.}$$

$$\text{II} \dots kR^2 = \text{Const.}$$

$$\text{V and IV} \dots vR = \text{Const.}$$

$$\text{VI} \dots \frac{kR^2}{\theta} = \text{Const.}$$

$$\text{VII} \dots \frac{kR}{T^3} = \text{Const.}$$

Now if the output is increased n -fold we have

$$v_h R_h^2 = n v_m R_m^2$$

where the subscript h refers to the full scale vessel and the subscript m refers to the model.

Combining these conditions above we see that

$$R_h = n R_m$$

$$v_h = \frac{1}{n} v_m$$

$$l_h = n l_m$$

$$k_h = \frac{1}{n^2} k_m$$

$$T_h = 3 \frac{1}{\sqrt{n}} T_m$$

Since the relationship between k_h and k_m (for homogeneous reactions at fixed pressure) also involves a relationship between T_h and T_m , viz.

$$e^{-b/T_h} = \frac{1}{n^2} e^{-b/T_m}$$

a condition of geometrical similarity with respect to the differential equations above can only be set up with one possible scale change and in most cases that change is very small. Take as a typical example $b=4,000$ and $T_h=800$. The allowed value of n then becomes 2.0 and n is less still if b/T_h is larger than 5. Thus the conditions for the attainment of complete similarity are not particularly useful if the same reaction is to be maintained on both scales. Thought must therefore be given to the usefulness of conditions of partial similarity (all the dimensionless parameters given above are not equally important in determining the efficiency of the chemical reaction, and under certain circumstances some may well be eliminated from practical considerations). Alternatively we may consider systems in which different reactions are used on the two scales. Two rules appear to emerge from the analysis above. *For combined reaction-kinetic and dynamical similarity it is necessary both that the flow rate and the chemical reaction rate should both be faster on the smaller scale reactor.*

More scope for the exploration of the method of chemical similarity is given by heterogeneous reactions. But again complete similarity demands embarrassing properties for the model system if the change in scale is large. Thus in general the catalyst grains in the model vessel should be larger than those in the full scale vessel and the catalyst activity higher on the smaller scale consonant with our finding above that the smaller scale reaction should be faster. It appears, therefore, that this subject is one requiring considerable detailed research before any great progress can be attained. A certain amount of progress is possible, however, by exploring the significance of some of the dimensionless ratios given above.

SIGNIFICANCE OF THE DIMENSIONLESS RATIOS.

The number I given in section (4) above is the ratio of the average life of a molecule under the conditions of the reaction to the average time taken to flow through the reaction vessel. The number II is the ratio of the average life of the molecules to the average time taken to diffuse across the reactor. I is obviously an expression for the efficiency of the reaction, II not so obviously. But whereas we may specify the average time of passage of the reaction vessel it is obvious that the molecule will spend different times in the reaction zone according to its distance from the wall and a complete description of the state of the system requires not only that we specify the average time of transit but also that we give the population curve, or frequency distribution curve from the reaction times (Bosworth, 1947). In the absence of diffusion the population

curves are easy to derive. In laminar flow the curve is that of an inverse cube, in turbulent flow roughly an inverse ninth power curve or more accurately

$$\frac{1 - \tau^{-8}}{\tau^8}$$

The effect of diffusion, which is the more pronounced the smaller the radius of the reaction vessel, tends to distort these distribution curves tending finally towards the shape of a law of errors curve. The dimensionless number II is the factor which determines the shape of the distribution curve.

The dimensionless quantity III, which clearly is of importance only for systems of a non-isomeric nature, is a measure of the ratio of the volume swept through by the reaction mixture in unit time to the volume increase in unit time consequent on chemical reaction. III thus is a measure of the hydrodynamical acceleration produced by chemical reaction which for a given reaction taking place at a given rate depends only on the time taken in passage through the reaction zone, viz. l/v .

The condition for thermodynamical similarity (VI) is the ratio of the heat developed by the chemical reaction in unit time to the heat removed by conduction in unit time. Similarly the quantity VII is the ratio of the reaction heat in unit time to the heat removed in unit time by the combined effects of radiation and of the convection arising from the volume changes produced by the reaction. Radiation and this natural convection are similar only in respect to the changes consequent on changes in the geometrical dimensions of the reaction vessel. With respect to changes in temperature they are, of course, entirely different. Quantities VI and VII are accordingly those factors which determine the magnitude of the temperature differences across the reaction mixture. The quantity V, like II, determines the shape of a distribution curve, this time for the temperature difference across the reaction mixture.

Quantity IV, the Reynolds number, determines the flow pattern and, in the turbulent zone, the magnitude of D_j (for turbulent diffusion) and λ (for turbulent conduction of heat).

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GEOLOGY OF THE ASHFORD COALFIELD.

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With Plate I and one Text-figure.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION AND ACKNOWLEDGEMENTS.

The Ashford Coalfield is so named from its occurrence adjacent to the town of Ashford. The coal measures outcrop in a narrow discontinuous belt from the vicinity of Bonshaw, on the Queensland border, to the neighbourhood of Inverell, a distance of approximately 50 miles. Known exposures of coal are confined to the County of Arrawatta.

Mr. D. G. Moye, B.Sc., assisted me on this survey, and his able cooperation is hereby gratefully acknowledged. The coal analyses were made in the Departmental Laboratory under the direction of Mr. E. N. Reidy, Chief Analyst.

The field work was carried out in the latter part of 1945. The positions of the various geological boundaries were mostly sketched in relationship to the nearest portion, lease or road boundary or by pace traverses. The survey in the vicinity of the Ashford Coal Mine was made with a telescopic alidade and plane table. A detailed plan of this area is filed in the Geological Survey Branch of the Department of Mines, together with a plan of M.L.I., Parish of Hallam, showing the positions of the shafts in that locality.

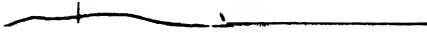
TOPOGRAPHY AND ACCESS.

The area is principally one of low and medium relief and the rivers mostly flow in fairly broad open valleys. The rougher country is confined mainly to areas of granite, particularly in the northern section, and to a lesser extent to the Carboniferous sedimentary rocks. The coal measures generally occupy valleys between hills formed of the other rocks.

The river system comprises the MacIntyre River, the Severn River, which flows into the MacIntyre, Frazer's Creek and their tributaries. It was developed prior to the eruption of the Tertiary basalts and although modified by these flows, the valleys probably occur in approximately the same positions as in pre-basalt time. In the vicinity of Bukkulla, the MacIntyre River and Frazer's Creek change their courses from north to north-west. Some miles further on they swing back and again follow a northerly course. This bend is probably a reflection of a sharp swing in the trend of the country rocks or of cross-faulting.

The nearest railhead in New South Wales is Inverell, which is 509 miles from Sydney by rail and 1,912 feet above sea level. Access by road is good, the coal measures always being less than two miles from a main road and never very far from the main road between Inverell and Bonshaw. Several of the roads shown on the County of Arrawatta as crossing the area are not trafficable, but roads of access could easily be constructed to any point where coal is likely to be found in commercial quantities.

Geological Map
ASHFORD COALFIELD
County of Arrawatta



1/1 III

GEOLOGY.

There have been numerous reports based on short visits to various parts of the Ashford Coalfield, but up to the present there has been no detailed geological survey of the whole field. David (1885) reported on coal at the site where the Ashford Coal Mine was subsequently opened. He also published a cross-section of the area in Memoir of the Geological Survey of N.S.W., Geology No. 4 (David, 1907). Pittman (1896) reported on parts of an area extending from south of the coal mine to the neighbourhood of Bonshaw. A report of a "Geological Reconnaissance of the Ashford Coalfield" was made by Jones in 1924.

The work described herein was confined, as far as possible, to tracing the limits of the Permian Coal Measures. Other rocks of the district were examined only in so far as was necessary to determine their general structure and relationships to the coal measures.

The geology of the district is shown in Figure 1. The rocks are now described, commencing with the sedimentary ones, taken in ascending stratigraphical order.

Carboniferous (?).

The oldest rocks in the district consist of a series of tuffs, tuffaceous grits, mudstones, shales, sandstones and cherts. These rocks were not mapped separately, but further work would probably disclose two main groups, one composed mainly of massive coarse tuffs with tuffaceous grits and sandstones, and another consisting mainly of thinly bedded mudstones, shales and cherts.

The rocks had been closely folded, probably faulted and subjected to considerable erosion prior to the deposition of the Permian Coal Measures. The strikes are mainly between N. 30° E. and N. 30° W. Dips measured are generally steep, varying from 30° to almost vertical, and in the large majority of cases are in an easterly direction, although in some places westerly dips are found.

Faulting of the sediments can be plainly seen in places, as for example along Spring Creek in the Parish of Alpine and along Reedy Creek in the Parish of McDonald. Whether the faults are pre- or post-coal measures it is impossible to say. Some at least must be post-coal measures, as the measures themselves show evidence of cross-faulting. The western boundary between the coal measures and the older sediments appears to be a faulted junction.

The age of these rocks has been the subject of much discussion, and the question cannot be regarded as finally settled. The only fossil evidence found during the survey was the cast of portion of a crinoid stem in the Parish of Ashford, adjacent to the town cemetery.

David (1893) and Pittman (1896) classified them as Carboniferous (Gympie). This classification was adhered to by them in a later report (David and Pittman, 1899), commenting on a paper by Dunn (1897). Jones (1924) also classified them as Carboniferous. Later David (1932) modified his views and placed the sediments in the Devonian. He was probably influenced in this decision by the similarity in lithology between these and the Barraba and Silverwood Series. The latter series outcrops across the border in Queensland, and has been described by Richards and Bryan (1924) as Devonian. David also regarded a belt of limestone about 10 miles north-west of Ashford as being Devonian and reported plant remains, considered by him to be *Lepidodendron* (?), from north of Bonshaw. Carey and Browne (1938) regarded these rocks as Devonian.

The Geological Survey of New South Wales has always considered the limestone to the west of Ashford as being Carboniferous. In 1940 Raggatt and others collected specimens of *Symplectophyllum mutatum* Hill (Raggatt, 1941), which Hill (1942) considers to be Upper Visean in age. Upper Visean fossils

have also been reported from the Texas-Bonshaw-Glen Lyon area of Queensland by Ball (1923), Bryan (1925) and Hill (1933, 1942).

In the absence of definite fossil evidence to the contrary, it is considered preferable not to change the view accepted previously by the Geological Survey as to the age of the older rocks of the Ashford Coalfield, especially as Carboniferous fossils are known to occur in nearby areas both on the New South Wales and Queensland sides of the border.

Carey and Browne (1938) consider that the Lower Kuttung and Upper Burindi Series are the Australian terrestrial and marine equivalents respectively of the European Viséan. They also consider that the pre-Permian rocks at Ashford were folded at the close of Burindi time during what they designate the Drummond movement and that there was no post-Upper Kuttung and pre-Permian orogeny in Queensland and New South Wales. The sediments in the Ashford district were heavily folded and subjected to considerable erosion prior to the deposition of the Permian Coal Measures, so this would place the end of Lower Carboniferous time as an upper limit to their deposition.

Permian.

Lower Coal Measures (?).

Pittman (1896), David (1907, 1932) and Jones (1924) regarded the Ashford Coal Measures as the equivalent of the Greta or Lower Coal Measures. Pittman (1896) records the occurrence of both *Gangamopteris* and *Glossopteris* in these beds.

The coal measures consist of a thin series of conglomerates, sandstones and shales containing a coal seam, which is up to 27 feet thick. They form a narrow discontinuous belt from Spring Gully in the Parish of Hallam, south-west of Bonshaw, at the northern end, to Byron, near Inverell, at the southern end.

The greatest width of outcrop measured was about 65 chains in the Parish of Arthur's Seat, between Ashford and Bukkulla. At this point the measures are apparently in the form of a syncline. This is the only locality from which easterly dips have been recorded in the coal measures.

The normal strike varies between N. and N. 30° E. with the dips westerly at between 30° and 40°. At Arrawatta, north of Inverell, a dip of about 55° in a direction N. 70° W. was recorded (Booker, 1941).

The greatest thickness of Permian sedimentary rocks measured was along the small gully described by Pittman (1896), about 70 chains south of the mine. Here they have a horizontal width of about 1,000 feet and dips measured varied between 30° and 35°. This would correspond to an actual thickness of the order of 550 feet. David (1930) quotes 510 feet as the thickness in the same locality. In the Cessnock-Greta and the Singleton districts the Greta Coal Measures are 200–250 feet thick. At Muswellbrook they are 645 feet thick (Raggatt, 1929), but the Skeletar Stage, which forms the lower 275 feet of the measures, is largely made up of rhyolite and rhyolite breccia, leaving 370 feet as the thickness of the sedimentary portion of the Lower Coal Measures. The development of an apparent thickness of 550 feet of Greta Coal Measures at Ashford, compared with 200–370 feet in the main areas of development, points to the possibility of either repetition due to faulting or the presence of Permian sediments other than Greta Coal Measures. Dunn (1897) refers to the occurrence of glacial conglomerate in the vicinity of the coal mine. This was refuted by David and Pittman (1899). However, David (1930) later reported the occurrence of glaciated pebbles from the same locality and was of the opinion that they may be referable to some part of the Upper Marine. Voisey (D.Sc. Thesis, unpublished) suggests that the Ashford sediments may be the terrestrial equivalents of Permian marine strata. It seems probable that the upper portion of the Permian at Ashford may be of Upper Marine age. If it could be definitely proved, it would preclude any

possibility of the Ashford Coal Measures being correlated with the Upper Coal Measures of the Newcastle district.

Coal has not been proved present at all points where the measures outcrop. However, as it has been proved at Spring Gully in the north and at Arrawatta in the south, and is 27 feet thick at the coal mine, it is reasonable to assume it will most likely be present wherever the measures outcrop.

The most northerly point of the area where coal has been proved is at Spring Creek in M.L.1, Parish of Hallam. Coal measures reputedly outcrop further north (Pittman, 1896), but the coal has not been proved. Two shafts have been sunk on the bank of Spring Creek. It was impossible to inspect either of the shafts which are at present in a state of disrepair. In the bank of the creek adjacent to the No. 1 or Old Shaft, the strike of the sediments appears to be about N. 40° W. and the direction of the dip S. 50° W. Near the No. 2 or Main Shaft the coal is not visible and the strike could not be determined. Further to the west the directions of dip of sediments, which probably form part of the coal measures, vary considerably. Due east along Spring Creek, at a point where the creek swings away to the north, the Carboniferous is faulted and it is possible that this faulting has affected the coal measures.

Along a tributary creek, south of Spring Creek, near the boundary of portions 11 and 12, Parish of Hallam, the coal measures are exposed and are bounded on the west by Carboniferous sediments. A chain or so further west the latter have been intruded by a tongue of granite.

It is probable that the coal measures extend in a general southerly direction from this locality, although no outcrops were seen until just north of Myall Creek. At this point coal measure conglomerate can be seen in the bank of Waterhole Creek.

There are no outcrops of the measures visible along Myall Creek, although outcrops of Carboniferous rocks are frequent. If the measures cross the creek the most likely spot for them to do so is the southern bend in portion 1, Parish of Ashby. Here the banks and bed of the creek are entirely in alluvial material.

It has been reported (Pittman, 1896) that after heavy floods on the Severn River, large masses of coal were found in the river adjacent to Frazer's Creek Homestead. It is probable, therefore, that the coal seam outcrops in the bed of the river, although it cannot be seen. The most likely position for the outcrop to occur is covered by a long and deep waterhole between portion 3, Parish of Ashby, and portion 1, Parish of McDonald.

The southern bank of the river is covered by alluvium and the coal measures are next found along and adjacent to T.S.R..28,605, in the vicinity of the coal mine, which has been opened up by means of an inclined shaft. This is the only area in the coalfield where any actual reserves have been proved. Nine bores were sunk recently and the results appear to indicate that the thickness of the seam increases in a southerly direction and at the same time the quality declines. The No. 9 bore, which is the most northerly, shows a thickness of coal of 20 feet, No. 8 bore 23 feet, the inclined shaft 27 feet, No. 5 bore 26 feet, and No. 3 bore, the most southerly, 33 feet. A considerable proportion of the seam in No. 3 bore apparently consists of poor quality coal and bands of shaly material, so that the seam may be splitting and deteriorating towards the south. On the other hand, this bore is close to a presumed cross fault and there may have been a certain amount of repetition in the bore due to faulting. The thicknesses quoted have been calculated by assuming that the dip of the seam in all cases is constant at 35° and that the bores are truly vertical through the seam.

The average strike of the coal seam over the length of more than three-quarters of a mile proved in the bores is N. 6° E. The strike in the inclined shaft is N. 30° E. and the dip is N. 60° W. at about 40°. The coal seam is underlain by a bed of conglomerate of varying thickness and is close to the base

of the measures. The proximity to the eastern boundary between the coal measures and Carboniferous sediments should facilitate the location of sites for bores or shafts in any future prospecting operations.

In a creek about 70 chains south of the mine shaft there is a good outcrop of the coal measures striking N. to N. 25° E. and dipping to the west at from 30° to 35°, but the seam itself is not visible. About 30 chains north of the point where the creek crosses the roadway, the outcrop of the coal measures takes a sharp swing to the west and has probably been faulted.

South of the creek referred to above, the coal measures do not outcrop for some distance but probably continue in a southerly direction through a saddle in the divide between the creek and one further south.

There is a considerable break in the continuity of the coal measures adjacent to the township of Ashford. There are no recognizable outcrops from about five miles north to about three miles south of the town, where an isolated outcrop of typical Permian conglomerate is showing in the bed of a small creek adjacent to the Ashford-Inverell road. It is bounded on the east and west by Carboniferous rocks.

South of Ashford, in the neighbourhood of Nine Mile Creek, is one of the most interesting areas in the coalfield. The northern section of the outcrop consists of a narrow belt of sediments and shows typical westerly dips. The southern section is much broader and there are dips both to the east and west. The rocks consist mainly of conglomerates, shales and sandstones and are apparently in the form of a syncline which pitches to the north off the Carboniferous basement. The coal seam is probably present, although no coal was seen.

The next known outcrop of the coal measures is near Arrawatta, about 13 miles further south. The measures outcrop along the bed and western bank of the MacIntyre River in portions 1 and 17, Parish of Champagne. The outcrop was examined by Booker (1941) and the writer at a time when the level of the MacIntyre River was very low owing to a prevailing drought. The coal measures outcrop over a length of approximately half a mile and consist of conglomerates, clay shales containing abundant plant remains, and a coal seam. The seam had been prospected many years ago by a shaft, allegedly 45 feet deep, in portion 4, Parish of Champagne, but details of the results are not known. During the drought in 1941 when the coal measures in the bed of the river were exposed, the coal was prospected by means of a costean and a shaft. The coal was exposed in the costean over a distance of 15 feet, being equivalent to an actual thickness of 10 feet. The vertical shaft 13 feet deep, sunk on the seam, exposed the lower six feet. A sample of this section gave the following analysis :

Hygroscopic moisture	4.02%
Volatile matter	10.14%
Fixed carbon	70.80%
Ash	15.04%
No coke formed.					
Ash : Buff, flocculent.					

The coal is underlain by a bed of white clay, the exact thickness of which is not known. A sample of this clay was tested by firing at 1450° C. and formed a good white stoneware, approaching china body quality. Soon after the inspection in 1941 the outcrops and prospecting openings were submerged and have not been exposed since. It is possible that extensions of the coal measures may be found under the river alluvium and basalt, but any prospecting through the latter would be very expensive.

The only other outcrop of coal measures seen during the course of the survey was on the western bank of the MacIntyre River within the surveyed town of DD—April 2, 1947.

Byron. An old map of the Parish of Byron, filed in the Geological Survey, shows coal outcropping in this vicinity, but no such outcrops were seen during the survey. The outcrop may have been noted at a time when the river was low and be submerged at the present time, as was the case at Arrawatta.

No outcrops of coal are known further south from the above. However, the area is apparently covered by basalt and a careful search of all creeks and gullies in the area, or the results of boring operations, may disclose further occurrences. The discovery of coal in this area would be important, both because of its proximity to rail and to the centre of the local demand at Inverell.

In most areas the coal measures are bounded on both the east and west by Carboniferous rocks. Along the eastern boundary the coal measures rest unconformably on the older rocks. The almost right-angled unconformity shows very well in Coal Gully adjacent to the coal mine shaft, and in the gully about 70 chains further south (see Plate I). At the latter site the gully runs parallel with the unconformable junction for about one chain.

The actual western boundary is not visible, but coal measures can be seen dipping westerly at about 30° within a chain of the Carboniferous rocks to the west. The most likely explanation is that the Carboniferous has been faulted against the coal measures. In the northern part of the Parish of Arthur's Seat and the southern part of the Parish of Ashford, the line of hills which is composed of Carboniferous rocks and represents the western and upthrow side of the fault is continuous between known outcrops of coal measures. Whether the fault is normal or overthrust is open to debate. The western boundary between the Carboniferous and coal measures in portion 58, Parish of Arthur's Seat, appears to be convex to the east between the tributaries of Nine Mile Creek, the Carboniferous rocks consisting partly of brecciated material. This would mean that the fault dips westerly and the fault would be an overthrust. However, in the absence of other confirmatory evidence it is impossible to be dogmatic. It is also noteworthy that there are several post-coal measure dykes of trachytic material in this locality, and the breccia may, at least in part, have resulted from this igneous activity.

The cross-faulting, referred to above, south of the mine, probably post-dates the fault forming the western boundary of the measures. The location has probably been influenced by the position of the tongue of granite which ends at the line of the fault.

The Ashford coal is much lower in volatile matter than other New South Wales Permian coals, the percentage varying between 10 and 25. It breaks up into small lenticular fragments and is considerably slickensided in places. Portions of the seam have a dull semi-coked appearance. Its nature infers alteration by considerable pressure and/or by adjacent igneous intrusions. The faulted western boundary of the coal measures proves that there has been considerable movement (and, if in the nature of an overthrust, considerable pressures developed) subsequent to the deposition of the coal measures.

Tertiary to Recent.

The deposits consist mainly of alluvium and eluvium, in part consolidated. They are very widespread throughout the area, although their depth is usually shallow and the mantle of weathered material would not exceed five to 10 feet in thickness in most instances. It is unfortunate that the nature of certain critical formation boundaries has to be inferred because they are obscured.

The different rock formations generally give rise to characteristic soils. The granites produce poor sandy soils, the basalts black, rich, clayey loams, which are so well developed around Inverell, and the Carboniferous sediments (locally known as "trap") form light-coloured loams. The soil derived from the coal

measures is least characteristic of all, being rather more sandy than those derived from the Carboniferous rocks and less sandy than those derived from the granites.

There is a small outcrop of sandstone and grit adjacent to the main Inverell-Bonshaw road, about half a mile north-west of Bukkulla. It was shown by David on an old parish map in the files of the Geological Survey as being of Tertiary age. Whether this determination was based on fossil evidence is not known. The outcrop was not examined in detail during the course of the present survey.

The Tertiary basalts are discussed below under the section on igneous rocks.

Igneous Rocks.

Granites.

The whole of the western margin of the area surveyed is occupied by granite. Two different types were collected. One, which in hand specimen closely resembles the tin granites of the New England, is pale-coloured and markedly porphyritic. Macroscopic examination shows that it consists of large phenocrysts of orthoclase and medium-sized phenocrysts of quartz in a groundmass of quartz, orthoclase, plagioclase, biotite and muscovite. The other is yellowish-pink in colour and much finer grained. There are no phenocrysts of orthoclase, although small quartz phenocrysts are common.

The porphyritic granite makes up the bulk of the intrusion and characteristically weathers into large bouldery wastes. The fine-grained type is only found along the eastern edge of the intrusion and is closely jointed, breaking into relatively small angular blocks upon weathering. In portion 46, Parish of Arthur's Seat, the Carboniferous rocks adjacent to the contact appear to be granitized. There was insufficient time on the present survey to study the internal structures of the granite mass, so that it is not possible to state whether the two types of granite represent two separate intrusions or whether the fine-grained type is a marginal phase of the porphyritic granite.

The age of the granite has never been definitely determined. It certainly intrudes the Lower Carboniferous (?) rocks and can definitely be regarded as post-Lower Carboniferous (?) as shown on Figure 1. The upper limit of the age is indefinite.

The main mass of the granite is situated to the west of and close to the coal measures and only isolated occurrences are found to the east. Outcrops are shown on the geological map of New South Wales east of Frazer's Creek, in the vicinity of Ashford and north-east of Bukkulla. A small outcrop near the village of Wandera is shown in Figure 1. A siliceous reef intrudes the Carboniferous near the eastern boundary of the coal measures and adjacent to the road, south of the coal mine. At most points along the western boundary of the coal measures there is a strip of Carboniferous rocks separating the measures from the granite. In the few places where there are no intervening rocks visible, the boundaries are obscured by waste. However, at no point was the granite seen to have actually intruded the coal measures. There is, therefore, no direct evidence that the granite was not pre-coal measures in age.* If it were as old as this it would probably have been intruded at the time of the Drummond orogeny. Under such circumstances any alteration of the coal would have been the result of compression during earth movements which gave rise to the faulting along the western edge of the present coal outcrop. On the other hand, the low volatile matter content of the coal may have been due to devolatilization caused by the granites being intruded subsequently to the coal measures being

* The writer has been informed that Professor David identified pebbles of granite in the Permian conglomerate (verbal communication from Dr. W. R. Browne). The possibility that these pebbles might have been derived from the adjacent granite strengthens the contention that it is pre-Permian in age.

laid down. The main mass of the porphyritic granite closely resembles the tin granites of New England, and these have been classified as Early Mesozoic by Andrews (1905) and as Late Permian by Browne (1929). The possibility of there being two separate intrusions of different age cannot be entirely overlooked.

The absence of definite evidence of the coal measures being intruded by the granite favours placing the age of the intrusion as pre-coal measures. However, the question has been left open for the present and the granite has been classified as post-Lower Carboniferous (?). Whatever the exact age, the intrusion shows a definite relationship to the structure of the country and the axis of injection of the granite and the direction of the strike of the fault forming the western boundary of the coal measures are closely related.

Basalts.

A large proportion of the southern half of the area is covered by Tertiary basalt flows. Easterly from Waterford's Creek the only outcrops of older rocks are along the MacIntyre River, Frying Pan Creek near Dinton Vale, and Vivers Gully near Wandera. On the other hand no outcrops of basalt were seen in the portion of the area north of the Parish of Arthur's Seat.

The basalts are typical of other Tertiary basalts found in New South Wales which have been described by Card (1903) and Browne (1933).

The basalts have been laterized in places. Some of these deposits have been described in connection with the survey of the bauxite resources of the State (Booker and Hanlon, 1944, Hanlon, 1944). Others occur near Oakwood and Dinton Vale. The Victorian aluminous laterites are either Lower Miocene or Lower Middle Miocene. It would take a considerable period for the formation of a laterite, so that if it is assumed that the laterization in New South Wales and Victoria was contemporaneous, it would make the basalts probably Oligocene or older in age.

The basalt flows probably modified the course of the MacIntyre River somewhat, but the valley is considered to occupy much the same position as in pre-basalt time. This question and the age of the basalt have been previously discussed more fully by the writer (Hanlon, 1944).

SUMMARY.

The coal measures at Ashford consist of a discontinuous belt over a distance of about 50 miles and have been laid down unconformably on Carboniferous (?) rocks. Except at one locality the dips in the coal measures are in a general westerly direction and the measures are apparently bounded on the west by a fault, probably in the nature of an overthrust. The Carboniferous (?) rocks have been intruded by granite. The granite may post-date the coal measures, although no evidence was seen that it intruded them. Oligocene (?) basalt flows have covered most of the southern portion of the area. Tertiary to Recent waste sheets, which are mostly thin, obscure most of the formation boundaries.

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EXPLANATION OF PLATE.

Fig. 1.—Northern face of Coal Gully, showing the almost right-angled unconformity between the Carboniferous (?), on the right of the photograph, and the Permian sediments. The junction is marked by a geological hammer.

Fig. 2.—Eastern bank of creek 70 chains to the south of Coal Gully. The geological hammer is on the unconformity between the Carboniferous (?), on the left of the photograph, and the Permian sediments.

OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1946.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

Manuscript received, February 3, 1947. Read, April 2, 1947.

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times either for personal effect or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the Nautical Almanac for 1938 and the reduction completed by the method given there. The necessary data were taken from the Nautical Almanac for 1946, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

Table I gives the observational material. The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table II gives the results of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the New Zodiacal Catalogue (Robertson, 1940) as recorded in the Nautical Almanac.

TABLE I.

Serial No.	N.Z.C. No.	Mag.	Date.	U.T.	Observer.
				h m s	
121	202	7.0	Mar. 6	9 13 31.2	R
122	469	7.3	Mar. 8	10 12 40.6	R
123	614	5.7	Mar. 9	8 56 55.4	W
124	1099	6.0	Mar. 12	10 44 27.6	W
125	1097	6.7	Mar. 12	10 49 34.2	W
126	1055	5.8	Apr. 8	8 26 23.3	R
127	1334	7.0	Apr. 10	10 22 53.3	R
128	1533	7.2	May 9	9 16 30.5	W
129	2097	7.1	July 8	13 08 23.2	W
130	1739	6.5	Aug. 1	9 23 49.6	W
131	1950	5.8	Aug. 3	9 24 30.8	W
132	2056	7.4	Aug. 4	9 39 32.3	W
133	2020	6.6	Aug. 31	10 24 55.8	W
134	2232	7.2	Sept. 2	9 58 36.8	R
135	2719	5.8	Oct. 3	9 42 45.8	W
136	3284	7.1	Oct. 7	13 56 27.2	W
137	2834	5.0	Oct. 31	12 39 38.4	W
138	2835	7.1	Oct. 31	12 50 55.0	W
139	3092	6.2	Nov. 2	12 38 50.6	W
140	3392	7.1	Dec. 29	11 56 19.4	W

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Robertson, A. J., 1940. *Astronomical Papers of the American Ephemeris*, Vol. X, Part II.

TABLE II.

Serial No.	Lunation.	p	q	p ²	pq	q ²	$\Delta\sigma$	p $\Delta\sigma$	q $\Delta\sigma$	Coefficient of	
										$\Delta\alpha$	$\Delta\delta$
121	287	97	+25	94	+24	6	"	"	"	+11.8	+0.62
122	287	+78	-63	60	-49	40	+0.6	0.0	0.0	+13.7	-0.33
123	287	+34	-94	12	-32	88	+1.6	+0.5	-0.4	-8.2	-0.81
124	287	+100	-7	100	-7	0	-0.4	+0.5	-1.5	-13.5	-0.11
125	287	+69	-72	48	-50	52	+1.1	-0.8	0.0	+9.0	-0.75
126	288	+97	+25	94	+24	6	-1.1	-1.1	-0.3	+13.1	+0.25
127	288	+100	-2	100	-2	0	-0.6	-0.6	0.0	+13.5	-0.23
128	289	+80	+60	64	+48	36	-2.6	-2.1	-1.6	+13.7	-0.29
129	291	+78	-62	61	-49	39	+0.4	+0.3	-0.2	+7.3	-0.87
130	292	+76	+65	58	+49	42	-2.5	-1.9	-1.6	+14.3	-0.27
131	292	+40	-92	16	-37	84	-2.6	+1.0	-2.4	-0.1	-1.00
132	292	+48	-88	23	-42	77	-2.6	-1.2	-2.3	+1.6	-1.00
133	293	+98	-22	95	-22	5	-1.4	-1.4	+0.3	-12.0	-0.59
134	293	+66	-75	44	-50	56	-0.2	-0.1	-0.2	+5.6	-0.92
135	294	+97	+25	94	+24	6	+0.2	-0.2	0.0	+13.2	+0.24
136	294	+94	-34	88	-32	12	-3.4	-3.2	-1.2	+14.3	0.00
137	295	+88	+47	78	+41	22	-0.9	-0.8	-0.4	+11.5	+0.53
138	295	+62	+78	39	-49	61	-0.6	-0.4	-0.5	+7.6	+0.83
139	295	+99	+11	99	-11	1	0.0	0.0	0.0	+13.1	-0.35
140	297	+59	+81	35	+48	65	-0.6	-0.4	-0.5	+3.2	+0.98

NOTE ON p-p'-DINITRO DIPHENYL DISULPHIDE.

By G. K. HUGHES
and E. P. O'LEARY.

Manuscript received, February 3, 1947. Read, April 2, 1947.

In consequence of a recent paper on the above subject to Price and Stacy (1946),* it was thought opportune to record the following observations which confirm their findings that the so-called second form of dinitro diphenyl disulphide is a mixture of disulphide, monosulphide and sulphur.

The crude disulphide (prepared by the standard methods) was treated with a solution of sodium sulphide, which converted any disulphide into the soluble sodium salt of p-nitro thiophenol. The residue was given a second treatment with sodium sulphide and then recrystallised from acetone as golden flakes melting at 158-9° C., indicating that it was p-nitro phenyl monosulphide.

This was confirmed by oxidation to the sulphoxide and sulphone and comparing the three products with those of authentic p-nitro phenyl sulphide, sulphoxide and sulphone. The latter compound was reported by Fromm and Wittman (1908) to melt at 282° C. and by Bennett and Youle (1938) at 251° C.; our product also melted at 251° C.

The presence of free sulphur in the crude disulphide was indicated by extraction with hot acetone, cooling and recrystallising the precipitated solid from acetone. Analysis gave a sulphur content of approximately 28%, which is much higher than that required by the disulphide.

It was, of course, the importance of p-nitro benzene sulphonyl chloride that directed attention to the above and a series of experiments on the chlorine oxidation of the disulphide in aqueous acetic acid was carried out in order to find the best conditions. It is recommended that less than 5% of water is the most convenient, although up to 20% of water does not alter the yield of product.

It was part of our original programme to attempt the preparation of the oxidation products of the disulphide, but one of us (E.P.O'L.) was unable to continue.

Two attempts by standard methods to prepare the -SO₂-S- compound were unsuccessful.

EXPERIMENTAL.

The crude disulphide was prepared by the method of Bell (1928).

Isolation of p-Nitro phenyl sulphide.

The crude disulphide (1 part) was refluxed with acetone (3 parts) and filtered hot, and from the cooled red solution a yellow solid m.p. 137-8° C. collected. To a boiling suspension of this substance (5 g.) in water (75 ml.) was added a solution of sodium sulphide (5 g.) in water (20 ml.). The insoluble residue was treated in a similar way with sodium sulphide (1 g.) in water (10 ml.), washed with water and alcohol and recrystallised from acetone as golden flakes m.p. 158-9° C., mixed m.p. with p-nitro phenyl sulphide (Nietzki and Bothot (1894)) 158-9° C.

* For a complete bibliography, see the paper by Price and Stacy.

p-Nitro phenyl sulphoxide.

This was prepared from the crude disulphide, the sulphide as isolated above and the authentic sulphide, as follows :

Chlorine was passed into a suspension of the substance (2 g.) in glacial acetic acid (10 ml.) for about ninety minutes ; water added and the white precipitate collected, washed well with water ; repeated recrystallisation from glacial acetic acid gave white needles, m.p. 178-9° C.

Found : N, 9.6 ; S, 11.0%.

Calculated for $C_{11}H_8N_2O_6S$: N, 9.6 ; S, 11.0%.

p-Nitro phenyl sulphone.

This was prepared from both the monosulphide and sulphoxide. The sulphide (1 g.) was dissolved in hot glacial acetic acid (10 ml.) and a solution of chromic acid (potassium dichromate (1.5 g.), water (20 ml.) and sulphuric acid (14 ml.)) was added gradually with stirring. After dilution with water, the solid was collected and recrystallised from glacial acetic acid as white feathery needles, m.p. 250-1° C. The yield in both cases was almost quantitative.

Chlorine Oxidation of Crude Disulphide.

This was carried out following the method of Loudon and Shulman (1938) with various percentages of water.

The sulphonyl chloride was estimated by titrating with alcoholic silver nitrate and ammonium thiocyanate.

Five grammes of crude disulphide were used in each experiment.

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A NEW METHOD OF APPROXIMATING THE BINOMIAL AND HYPERGEOMETRIC PROBABILITIES.

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I. THE BINOMIAL CASE.

Let P_r denote the probability of exactly r successes in n trials if at each trial the probability of a success is p . Instead of using Stirling's formula and expanding $\log_e P_r$ in powers of n^{-1} , as originated by De Moivre and Laplace (Todhunter, §§333, 993), the idea is to expand $\log_e \frac{P_{r+1}}{P_r}$, which is $\Delta \log_e P_r$; then to derive $\frac{d}{dr} \log_e P_r$ by means of such formulas as (Boole, pp. 25, 89)

$$f'(x) = \Delta f(x) - \frac{1}{2} \Delta^2 f(x) + \frac{1}{3} \Delta^3 f(x) - \dots \quad (1)$$

$$f'(x) = \left(1 - \frac{1}{2} \frac{d}{dx} + \frac{1}{12} \frac{d^2}{dx^2} - \dots \right) \Delta f(x) \quad (2)$$

the interval being 1; and to solve the simple differential equation.

This is less direct than the classical procedure, but the algebra is less cumbrous, the construction of the expansion is clearer, and choice of terms for various orders of approximation is made more easily.

We shall take $p < q$, as the same analysis is applicable in the complementary case of the number of failures $s (= n - r)$ if $q < p$. We have $P_{r+1}/P_r = \frac{n-r}{r+1} \cdot \frac{p}{q}$, where $q = 1 - p$, or, putting $r = np + x$, and writing P_x for P_r to indicate the substitution, $P_{x+1}/P_x = \frac{p(nq - x)}{q(np + x + 1)} = \frac{1 - px/v}{1 + q(x+1)/v}$, where $v = npq \dots \dots (3)$

Expanded in powers of (v^{-1}) ,

$$\begin{aligned} \log P_{x+1} - \log P_x = & -\frac{px}{v} - \frac{p^2 x^2}{2v^2} - \frac{p^3 x^3}{3v^3} - \dots \\ & - \frac{q(x+1)}{v} + \frac{q^2(x+1)^2}{2v^2} - \frac{q^3(x+1)^3}{3v^3} + \dots \dots \dots (4) \end{aligned}$$

$$\begin{aligned} \text{or } \Delta \log P_x = & -\frac{(q+p)x+q}{v} + \frac{(q^2-p^2)x^2+q^2(2x+1)}{2v^2} \\ & - \frac{(q^3+p^3)x^3+q^3(3x^2+3x+1)}{3v^3} + \dots \dots \dots (5) \end{aligned}$$

When r is near np , i.e. when x is $O(1)$, both terms (distinguished according to powers of x) of the first group are $O(v^{-1})$, the three terms of the second group are $O(v^{-2})$, and so on. When $|x|$ increases to $O(v^{\frac{1}{2}})$, the terms of the successive groups are $O(v^{-\frac{1}{2}}, v^{-1})$, $O(v^{-1}, v^{-\frac{3}{2}}, v^{-2})$, and so on.

For values of x ranging from $O(1)$ to $O(v^{\frac{1}{2}})$ we may then evaluate $\Delta \log P_x$ with various degrees of approximation, by neglecting terms of (5) which are of higher than a specified order of smallness *throughout* this range of x .

First Approximation to P_x .

Neglecting terms of order higher than $O(v^{-\frac{1}{2}})$, we have

$$\Delta \log P_x = -\frac{(q+p)x}{v} = -\frac{x}{v} \dots \dots \dots (6)$$

$$\Delta^2 \log P_x = -\frac{1}{v} = 0 \quad \text{to } O(v^{-\frac{1}{2}}), \text{ and } \Delta^3 \log P_x = 0.$$

$$\text{Hence by (1), } \frac{d}{dx} \log P_x = -\frac{x}{v} \text{ to } O(v^{-\frac{1}{2}}) \dots \dots \dots (7)$$

$$\text{and } P_x = h \exp \left(-\frac{x^2}{2npq} \right), \text{ } h \text{ being a constant of integration } \dots \dots \dots (8)$$

Second Approximation to P_x .

Neglecting terms of order above $O(v^{-1})$, we have

$$\Delta \log P_x = -\frac{x+q}{v} + \frac{(q-p)x^2}{2v^2} \dots \dots \dots (9)$$

$$\Delta^2 \log P_x = -\frac{1}{v}, \text{ as } \frac{(q-p)(2x+1)}{2v^2} \text{ is } O(v^{-\frac{3}{2}}) \text{ at lowest,}$$

$$\Delta^3 \log P_x = 0.$$

$$\begin{aligned} \text{Hence by (1), } \frac{d}{dx} \log P_x &= -\frac{x+q}{v} + \frac{1}{2v} + \frac{(q-p)x^2}{2v^2} \\ &= -\frac{x}{v} - \frac{q-p}{2v} \left(1 - \frac{x^2}{v} \right) \text{ to } O(v^{-1}) \dots \dots \dots (10) \end{aligned}$$

$$\text{and } P_x = k \exp \left[-\frac{x^2}{2v} - \frac{q-p}{2v} \left(x - \frac{x^3}{3v} \right) \right], \text{ } k \text{ being a constant; or,}$$

writing $t = \frac{x}{\sqrt{v}} = \frac{r-np}{\sqrt{npq}}$, which is $O(1)$ when x is $O(v^{\frac{1}{2}})$,

$$P_t = k \exp \left[-\frac{1}{2}t^2 - \frac{q-p}{2\sqrt{v}} \left(t - \frac{1}{3}t^3 \right) \right] \dots \dots \dots (11)$$

$$= ke^{-\frac{1}{2}t^2} \left\{ 1 - \frac{q-p}{2\sqrt{v}} \left(t - \frac{1}{3}t^3 \right) \right\} \dots \dots \dots (12)$$

In deriving (12) from (11) we neglect terms $O(v^{-1})$ in the expansion of $\exp \left[-\frac{q-p}{2\sqrt{v}} \left(t - \frac{1}{3}t^3 \right) \right]$, for to retain them would be equivalent to retaining terms $O(v^{-\frac{1}{2}})$ in (10). As may be anticipated, it will presently appear that k is $O(v^{-\frac{1}{2}})$, and therefore that (12) is an approximation to $O(v^{-1})$ as intended.

To determine the constant k , we have, assuming that (12) is effective throughout the range of x ,

$$1 = \sum_{r=0}^n P_r = \sum_{x=-np}^{nq} P_x = \sum_{t=-np/\sqrt{v}}^{nq/\sqrt{v}} P_t, \text{ the interval for } t \text{ being } 1/\sqrt{v}. \text{ Hence}$$

by an Euler-Maclaurin formula (Milne-Thomson, p. 190),

$$1 = \sqrt{v} \int_{-(np+\frac{1}{2})/\sqrt{v}}^{(nq+\frac{1}{2})/\sqrt{v}} P_t dt - \frac{1}{24\sqrt{v}} \left\{ \frac{P'}{(nq+\frac{1}{2})/\sqrt{v}} - \frac{P'}{-(np+\frac{1}{2})/\sqrt{v}} \right\} + \dots \quad (13)$$

In such a case as $n=20$, $p=0.3$, $q=0.7$, we have $np=6$, $nq=14$, $v=npq=4.2$, $\sqrt{v}=2.05$, and from (12) the integral in (13) is

$$k\sqrt{(2\pi v)} \left[\frac{1}{\sqrt{2\pi}} \int e^{-\frac{1}{2}t^2} dt + \frac{(q-p)(1-t^2)}{6\sqrt{v}} \cdot \frac{e^{-\frac{1}{2}t^2}}{\sqrt{2\pi}} \right]_{-3.17}^{7.1} \dots \quad (14)$$

From K. Pearson's tables of areas and ordinates of the normal frequency curve, it appears that the value of the first term in the square bracket is 0.9992, of the second, 0.0008, and of the second term in (13), less than 0.0001. So in this case k is sensibly $\frac{1}{\sqrt{(2\pi v)}}$. Likewise if $n=100$, $p=0.1$, then $np=10$,

$v=npq=9$, $\sqrt{v}=3$, and the apparent error of taking $\frac{1}{\sqrt{(2\pi v)}}$ for the constant is of similar magnitude.

So for quite moderate values of npq such as often occur in practice, we are led to the well-known formula (Uspensky, p. 135, Ex. 7),

$$P_r = \frac{1}{\sqrt{(2\pi npq)}} e^{-\frac{1}{2}t^2} \left\{ 1 - \frac{(q-p)(3t-t^3)}{6\sqrt{(npq)}} \right\} \text{ where } t = \frac{r-np}{\sqrt{(npq)}} \dots \quad (15)$$

The practising statistician is most interested in areas of tails in order to estimate "significance levels." The probability that $r \leq r_1$ is $\sum_{r=0}^{r_1} P_r$ and $\sum_{r=0}^{r_1} P_r = \frac{1}{\sqrt{2\pi}} \left[\int e^{-\frac{1}{2}t^2} dt + \frac{(q-p)(1-t^2)}{6\sqrt{(npq)}} e^{-\frac{1}{2}t^2} \right]_{-\infty}^{t_1}$, where $t_1 = (r_1 + \frac{1}{2} - np)/\sqrt{(npq)}$, and for $r \geq r_2$ the limits are $(r_2 - \frac{1}{2} - np)/\sqrt{(npq)}$ and ∞ (16)

When r_1 and r_2 are equidistant from np or nearly so, and $r_1 < np < r_2$, the sum of these probabilities is $1 - \frac{2}{\sqrt{2\pi}} \int_0^{t_m} e^{-\frac{1}{2}t^2} dt$ nearly, where t_m is the mean of

the absolute values of the finite limits. This is equivalent to Laplace's form (Uspensky, p. 130), and in practice is regarded as giving the significance level usually with sufficient accuracy, provided that we define "significance level" in the case of discrete distributions as the sum of the probabilities of values which are about as probable as, or less probable than, the observed value, and find by means of (15) the best companion value r_2 to go with an observed r_1 , and *vice versa*.

Accuracy of the Approximate Evaluation.

If, as in (14), the lower limit $-(np + \frac{1}{2})/\sqrt{v} \geq \sqrt{10}$, there is no difficulty in confirming $1/\sqrt{(2\pi v)}$ within a few units per 1,000 as the constant appropriate to the second approximation. Supposing this limitation accepted, we

should have $\frac{n^2 p^2 + np + \frac{1}{4}}{np} \geq 10(1-p)$, or $p \geq \frac{9}{n+10}$ nearly (17)

But, of course, fulfilment of this, or a more, or less, stringent condition, would not imply a corresponding degree of accuracy in the approximate formula. For example, if $n=8$, $p=\frac{1}{2}$, it may be verified as in (14) that the derived constant differs from $1/\sqrt{(2\pi v)}$ by less than 2 per 1,000, but the errors committed by using the approximate formula range from 0.001 to 0.008 in absolute value.

Professor J. V. Uspensky, in his Chap. 7, emphasizes the importance of knowing how large an error may be committed and gives several upper limits. For the error E in P_r as computed from (15) herein, he finds (Uspensky, p. 135)

$$|E| < \frac{0.15 + 0.25 |q-p|}{(npq)^{\frac{3}{2}}} + e^{-\frac{3}{2}} \sqrt{(npq)}, \text{ provided } npq > 25 \dots (18)$$

As the proviso indicates, this formula is not suitable for cases in which npq is comparatively small. In the case above mentioned where $n=8$, $p=\frac{1}{2}$, $npq=2$, it gives $|E| < 0.17$, which is about 20 times the actual maximum error committed. It is possible, however, to deduce from higher approximations to P_r closer limits than the above for the errors committed by using the classical second approximation.

Denoting by $P_r^{(s)}$ the value of P_r obtained by the s th approximation, we may first note that by (8) and (15)

$$E_1 \equiv P_r^{(1)} - P_r^{(2)} = \frac{1}{\sqrt{(2\pi npq)}} e^{-\frac{1}{2}t^2} \frac{(q-p)(3t-t^3)}{6\sqrt{(npq)}} \text{ where } t = \frac{r-np}{\sqrt{(npq)}} \dots (19)$$

Differentiating with regard to t , we find critical points for E_1 at $t^2 = 3 \pm \sqrt{6}$ and, using the tables, that the lower sign gives the numerical maximum.

$$\text{Hence } |E_1| < \frac{0.1 |q-p|}{npq} \dots (20)$$

Third Approximation to P_r .

Some little advantage is gained in the higher approximations if we side-track the calculation of Δ^2 , Δ^3 , . . . by using (2) instead of (1).

Applying (2) to (4) we have

$$\frac{d}{dx} \log P_x = \sum_{s=1}^{\infty} \left\{ -\frac{p^s B_s(x)}{v^s s} + \frac{q^s B_s(x+1)}{(-v)^s s} \right\}.$$

$$\text{Hence } \log P_x = C + \sum_{s=1}^{\infty} \left\{ -\frac{p^s B_{s+1}(x)}{v^s s(s+1)} + \frac{q^s B_{s+1}(x+1)}{(-v)^s s(s+1)} \right\}, \dots (21)$$

where the constant elements of Bernoulli's polynomials $B_s(x)$, etc., are now absorbed in C . (In virtue of the property $\Delta B_r(x) = rx^{r-1}$, (21) may be written direct from the difference equation (4).) Noting that $B_r(x+1) =$

$B_r(x) + rx^{r-1}$ (Milne-Thomson, pp. 136-141) we have

$$P_x = K \exp \left\{ \frac{-p(x^2 - x) - q(x^2 + x)}{2v} + \frac{-p^2\left(x^3 - \frac{3}{2}x^2 + \frac{1}{2}x\right) + q^2\left(x^3 + \frac{3}{2}x^2 + \frac{1}{2}x\right)}{6v^2} \right. \\ + \frac{-p^3(x^4 - 2x^3 + x^2) - q^3(x^4 + 2x^3 + x^2)}{12v^3} \\ + \frac{-p^4\left(x^5 - \frac{5}{2}x^4 + \frac{5}{3}x^3 - \frac{1}{6}x\right) + q^4\left(x^5 + \frac{5}{2}x^4 + \frac{5}{3}x^3 - \frac{1}{6}x\right)}{20v^4} \\ \left. + \frac{-p^5\left(x^6 - 3x^5 + \frac{5}{2}x^4 - \frac{1}{2}x^2\right) - q^5\left(x^6 + 3x^5 + \frac{5}{2}x^4 - \frac{1}{2}x^2\right)}{30v^5} + \dots \right\}$$

and putting $t = xv^{-\frac{1}{2}} = \frac{r-np}{\sqrt{npq}}$,

$$P_r = K \exp \left\{ \frac{-(q+p)t^2}{2} + \frac{-3(q-p)t + (q^2 - p^2)t^3}{6v^{\frac{1}{2}}} + \frac{3(q^2 + p^2)t^2 - (q^3 + p^3)t^4}{12v} \right. \\ + \frac{5(q^2 - p^2)t - 10(q^3 - p^3)t^3 + 3(q^4 - p^4)t^5}{60v^{\frac{3}{2}}} \\ + \frac{-10(q^3 + p^3)t^2 + 15(q^4 + p^4)t^4 - 4(q^5 + p^5)t^6}{120v^2} \\ \left. + \dots \right\} \dots \dots \dots (22)$$

The first two terms are those required for the second approximation already dealt with. The next is additional for the third approximation, the following for the fourth, and so on. The alternation in sign of $(q^h \mp p^h)$ according to odd and even powers of t and $v^{\frac{1}{2}}$ is noteworthy.

$$\text{Putting } g = q - p, \text{ we have } q^h \pm p^h = \frac{1}{2^h} \{(1+g)^h \pm (1-g)^h\} \dots \dots \dots (23)$$

and for the third approximation

$$P_r^{(3)} = K \exp \left\{ -\frac{1}{2}t^2 - \frac{g(3t - t^3)}{6v^{\frac{1}{2}}} + \frac{6(1+g^2)t^2 - (1+3g^2)t^4}{48v} \right\} \\ = Ke^{-\frac{1}{2}t^2} \left\{ 1 - \frac{g(3t - t^3)}{6v^{\frac{1}{2}}} + \frac{\frac{3}{2}g^2(3t - t^3)^2 + 6(1+g^2)t^2 - (1+3g^2)t^4}{48v} \right\} \\ \dots \dots \dots (24)$$

to $O(v^{-1})$ in $\{ \}$, i.e. to $O(v^{-\frac{1}{2}})$ in $P_r^{(3)}$.

Determining the constant as in (13), (14), we have

$$\frac{1}{K} = \sqrt{(2\pi v)} \left\{ 1 + \frac{\frac{3}{2}g^2(9 - 18 + 15) + 6(1+g^2) - 3(1+3g^2)}{48v} \right\}$$

$$\text{or } K = 1 / \left\{ \left(1 + \frac{3-g^2}{48v} \right) \sqrt{(2\pi v)} \right\} \dots \dots \dots (25)$$

Recalling that $P_r^{(2)} = \frac{1}{\sqrt{(2\pi v)}} e^{-\frac{1}{2}t^2} \left\{ 1 - \frac{g(3t-t^3)}{6v^{\frac{1}{2}}} \right\}$, we have to $O(v^{-\frac{1}{2}})$
 $E_2 = P_r^{(2)} - P_r^{(3)}$

$$= \frac{1}{\sqrt{(2\pi v)}} e^{-\frac{1}{2}t^2} \cdot \frac{1}{48v} \{ 3 + g^2 - \frac{2}{3}g^2(3t-t^3)^2 - 6(1+g^2)t^2 + (1+3g^2)t^4 \} \dots \dots \dots (26)$$

or $E_2 = \frac{e^{-\frac{1}{2}t^2} F}{48v^{\frac{1}{2}} \sqrt{2\pi}}$, where $F = (3 - 6t^2 + t^4) + g^2(1 - 12t^2 + 7t^4 - \frac{2}{3}t^6)$
 $= A + g^2 B$.

Differentiating, we find that A has critical values at $t=0$, $t^2=3$, and B at $t=0$, $t^2=1$, 6 . The course of E_2 may be examined in the following schedule, which shows that only when g^2 is nearly 1 is there a value of t^2 , viz. 1 nearly, which vies with $t=0$ to produce the numerical maximum value of E_2 .

$$\text{Hence } |E_2| < \frac{0.399(3+g^2)}{48v^{\frac{1}{2}}} \times \frac{1.624}{1.596} < \frac{0.0254\{1 + \frac{1}{3}(q-p)^2\}}{(npq)^{\frac{1}{2}}}, \dots \dots \dots (27)$$

where the decimal may be read as 0.025 for all cases in which $p > 0.01$.

Schedule of Elements of Value of E_2 .

t^2	t	$\frac{e^{-\frac{1}{2}t^2}}{\sqrt{2\pi}}$	A	B	$\frac{(A+B)e^{-\frac{1}{2}t^2}}{\sqrt{2\pi}}$
0	0	0.399	3	1	1.596
.25	.5	.352	1.56	-1.57	
.55	.742	.304	0	-3.59	
.90	.949	.254	-5.94	-4.62	-1.576
.95	.975	.248	-1.80	-4.65	-1.600
1.0	1.0	.242	2.0	-4.67	-1.613
1.05	1.025	.236	-2.20	-4.65	-1.617
1.1	1.049	.230	2.39	-4.62	-1.612
2.0	1.414	.147	-5.0	-0.33	
3.0	1.732	.089	-6.0	10.0	
3.5	1.872	.070	-5.8	16.2	
4.0	2.0	.054	-5.0	22.3	
5.0	2.235	.033	-2.0	32.7	
6.0	2.450	.020	3.0	37.0	
7.0	2.636	.013	10.0	35.8	

Further Approximations to P_r .

Applying (23), we may write (22) as

$$P_r = K \exp \left\{ -\frac{1}{2}t^2 + av^{-\frac{1}{2}} + bv^{-1} + cv^{-\frac{3}{2}} + dv^{-2} + \dots \right\}$$

where $a = -\frac{1}{6}g(3t-t^3)$,

$$b = \frac{1}{48} \{ 6(1+g^2)t^2 - (1+3g^2)t^4 \}$$

$$c = \frac{1}{120} g \{ 10t - 5(3+g^2)t^3 + 3(1+g^2)t^5 \}$$

$$d = \frac{1}{960} \{ -20(1+3g^2)t^2 + 15(1+6g^2+g^4)t^4 - 2(1+10g^2+5g^4)t^6 \} \dots \dots \dots (28)$$

Expanding $\exp(av^{-\frac{1}{2}} + bv^{-1} + cv^{-\frac{3}{2}} + dv^{-2} + \dots)$, we have

$$P_r = Ke^{-\frac{1}{2}t^2} \left\{ 1 + av^{-\frac{1}{2}} + \left(\frac{1}{2}a^2 + b \right) v^{-1} + (ab + \frac{1}{2}a^3 + c) v^{-\frac{3}{2}} + \left(ac + \frac{1}{2}a^2b + \frac{1}{24}a^4 + \frac{1}{2}b^2 + d \right) v^{-2} + \dots \right\} \dots \dots (29)$$

As the terms with odd powers of $v^{-\frac{1}{2}}$ involve only odd powers of t , the constant for $P^{(2)}$ is the same as for $P^{(1)}$, as already noted, and now the constant for $P^{(4)}$ is the same as for $P^{(3)}$, viz. from (25), $1/(1 + hv^{-1})\sqrt{(2\pi v)}$, where $h = \frac{3+g^2}{48}$.

We further calculate the constant for $P^{(5)}$ as $1/(1 + hv^{-1} + \frac{1}{2}h^2v^{-2})\sqrt{(2\pi v)}$, which, to the order calculated, is $e^{-\frac{1}{2}t^2}(2\pi v)^{-\frac{1}{2}} \dots \dots \dots (30)$

Hence, writing Y for $e^{-\frac{1}{2}t^2}(2\pi v)^{-\frac{1}{2}}$, we have successively,

$$P^{(1)} - P^{(2)} = -Yav^{-\frac{1}{2}} \text{ to } O(v^{-1})$$

$$P^{(2)} - P^{(3)} = -Y(\frac{1}{2}a^2 + b - h)v^{-1} \text{ to } O(v^{-\frac{3}{2}}) \text{ which have been calculated above;}$$

$$P^{(3)} - P^{(4)} = -Y(ab + \frac{1}{2}a^3 + c - ha)v^{-\frac{3}{2}} \text{ to } O(v^{-2}), \text{ and}$$

$$P^{(4)} - P^{(5)} = -Y \left(ac + \frac{1}{2}a^2b + \frac{1}{24}a^4 + \frac{1}{2}b^2 + d - h(\frac{1}{2}a^2 + b) + \frac{1}{2}h^2 \right) v^{-2} \text{ to } O(v^{-\frac{5}{2}}) \dots \dots \dots (31)$$

$$\text{Examining } E_3 \equiv P^{(3)} - P^{(4)} \text{ as above, we find } |E_3| < \frac{0.02 |q-p|}{(npq)^2} \dots \dots \dots (32)$$

Summary of Limits.

It is not an object of this paper to find upper limits of error in order to prove Bernoulli's theorem rigidly. This has been done by Professor Uspensky. The idea is merely to find close and convenient limits for use by the practising

statistician. Three limits are available: $|E_1| \equiv |P_r^{(1)} - P_r^{(2)}| < \frac{0.1 |q-p|}{npq}$,

$$|E_2| \equiv |P_r^{(2)} - P_r^{(3)}| < \frac{0.0254 \{1 + \frac{1}{2}(q-p)^2\}}{(npq)^{\frac{3}{2}}}, |E_3| \equiv |P_r^{(3)} - P_r^{(4)}| < \frac{0.02 |q-p|}{(npq)^2}.$$

E_4 might, doubtless, be expressed as a function of $(q-p)$, but it may suffice to find its maximum when $q=1$ (the Poisson case, which gives the largest errors),

$$\text{which occurs when } t^2 = 1.66. \text{ Hence } |E_4| \equiv |P_r^{(4)} - P_r^{(5)}| < \frac{0.016}{(npq)^{\frac{5}{2}}}.$$

Because the numerically greatest values of E_1, E_2, E_3 occur at different values of t , e.g. when $q=1$, at $t^2=0.55, (0 \text{ and } 1.05), 1.38$ respectively, the limits are not additive, and so $|P_r^{(1)} - P_r^{(3)}| < |E_1| + |E_2|$ and so on. This might, of course, be remedied if thought necessary, by considering maximum values of $e^{-\frac{1}{2}t^2}F$, where F contains both odd and even powers of t , but the disjointed method by which F contains either odd or even powers presents a simpler task.

The error of the classical approximation is, perhaps, of the greatest interest. In all cases calculated by the writer, except those where p is very small, the formula for E_2 gives a true and close upper limit. For example, when (a) $n=20, p=0.3, npq=4.2$; (b) $n=100, p=0.1, npq=9$; (c) $n=8, p=0.5, npq=2$; (d) $n=100, p=0.5, npq=25$; the maximum error of P_r is covered by the formula for $|E_2|$. In this last case the Uspensky formula gives nearly nine times the maximum. It is also noted by the way, that, in this case, the

third approximation to P_r ((24) with constant (25)), gives P_r with an error < 0.00001 . On the other hand, for $n=1256$, $p=0.005$, $npq=6.25$, the formula gives $|E_2| < 0.0022$, whereas the actual maximum error is 0.0023 . This is easily covered by including $|E_3|$.

II. THE HYPERGEOMETRIC CASE.

This is the realistic statistical case of sampling from a finite population without replacement. From a population consisting of Np ayes and Nq noes a random sample of n is drawn. Denoting by P_r the probability that the sample

contains exactly r ayes, we have $P_r = \binom{Np}{r} \cdot \binom{Nq}{n-r} / \binom{N}{n}$

Hence $P_{r+1}/P_r = \frac{n-r}{r+1} \cdot \frac{Np-r}{Nq-n+r+1}$, which, when N is large in comparison

with n , approximates to the binomial form $\frac{(n-r)p}{(r+1)q}$ treated above. To include

cases when N and n are comparable, by putting $r=np+x$, $v=npq$, $w=(N-n)pq$,

we have $P_{r+1}/P_r = \frac{1-px/v}{1+q(x+1)/v} \cdot \frac{1-qx/w}{1+p(x+1)/w}$. Proceeding as in I, we find,

in parallel with the expression following (10), for the second approximation to P_r ,

$$P_r = k \exp \left[-\frac{x^2}{2npq} - \frac{q-p}{2npq} \left(x - \frac{x^3}{3npq} \right) - \frac{x^2}{2(N-n)pq} + \frac{q-p}{2(N-n)pq} \left\{ x - \frac{x^3}{3(N-n)pq} \right\} \right] \dots \dots \dots (33)$$

the lower line of the exponential being obtainable from the upper by substituting $(N-n)$ for n and interchanging p and q , and k being a constant to be determined. Hence

$$P_r = k \exp \left[-\frac{x^2}{2pqn \left(1 - \frac{n}{N} \right)} - \frac{(q-p)}{2pq} \left\{ \frac{x \left(1 - \frac{2n}{N} \right)}{n \left(1 - \frac{n}{N} \right)} - \frac{x^3 \left(1 - \frac{2n}{N} \right)}{3pqn^2 \left(1 - \frac{n}{N} \right)^2} \right\} \right] \dots \dots \dots (34)$$

Writing σ for $\sqrt{\{npq \left(1 - \frac{n}{N} \right)\}}$ and t for $\frac{x}{\sigma}$, this becomes after expanding the second term of the exponential,

$$P_r = k e^{-\frac{1}{2}t^2} \left\{ 1 - \frac{(q-p) \left(1 - \frac{2n}{N} \right)}{2\sigma} \left(t - \frac{1}{3}t^3 \right) \right\} \dots \dots \dots (35)$$

which differs in form from the corresponding binomial expression (12) only through the factor $\left(1 - \frac{2n}{N} \right)$ in the correction term.

As for the constant k , the conditions for finding that this should be sensibly $\frac{1}{\sigma\sqrt{2\pi}}$ where $\sigma = \sqrt{\left\{npq\left(1 - \frac{n}{N}\right)\right\}}$, are the more easily fulfilled as the present σ is less than $\sqrt{(npq)}$, its value in the binomial case. For example, to correspond with (17), viz. $p > \frac{9}{n+10}$ nearly, we now have $p > \frac{9-10n/N}{n+10-10n/N}$ (36) which in the case of a 30% sample is $6/(n+7)$.

The cumulative probability corresponding to (16) for the binomial case is

$$\sum_{r=0}^{r_1} P_r = \frac{1}{\sqrt{2\pi}} \left[\int_{-\infty}^{t_1} e^{-\frac{1}{2}t^2} + \frac{(q-p)\left(1 - \frac{2n}{N}\right)}{\sigma\sqrt{\left\{npq\left(1 - \frac{n}{N}\right)\right\}}} (1-t^2)e^{-\frac{1}{2}t^2} \right] \dots\dots\dots (37)$$

where $t_1 = (r_1 + \frac{1}{2} - np) / \sqrt{\left\{npq\left(1 - \frac{n}{N}\right)\right\}}$.

The error limits for the hypergeometric P_r as well as for "significance levels" for both cases, and the reason why the modern French approximation (Borel, p. 45) is inferior to Laplace's may be the subjects of a further paper.

It may be noted that the expansion of the binomial P_r may be written

$$P = P^{(1)} + (P^{(2)} - P^{(1)}) + (P^{(3)} - P^{(2)}) + \dots$$

where $P^{(1)} = (2\pi v)^{-\frac{1}{2}} e^{-\frac{1}{2}t^2}$ and the bracketed terms have the values given by (31). It can be verified that this series agrees with H. Cramér's asymptotic expansion (Cramér, p. 87). For example, in the line following (26) we have

$$F = H_4(t) - g^2\{3H_4(t) + \frac{5}{2}H_6(t)\}$$

where $H_4(t)$ and $H_6(t)$ are the 4th and 6th Hermite polynomials. The 3rd and 4th semi-invariants of the binomial distribution being $K_3 = vg$ and $K_4 = -\frac{1}{2}v(1-3g^2)$, it follows that $(P^{(3)} - P^{(2)})$ agrees with Cramér's $P_{2n}(-\Phi)$, and so on.

On the other hand, the Type A series (Charlier, Bruns, Gram and Thiele) gives for this term $(1-3g^2)H_4(t)$, the portion involving $H_6(t)$ being deferred (Cramér, p. 88), and it is found that differentiation of the expression for $(P^{(3)} - P^{(2)})$ thus truncated does not closely locate that value of t which shows the greatest numerical error, as does equivalent treatment of the full expression. So it appears that in the case of the binomial asymptotic expansion, if $q \neq p$, the rearrangement of terms involved in the simpler Type A form (Rietz, p. 158) retards the convergency.

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CORRIGENDUM.

In the present writer's paper "Elementary Presentation of the Frequency Distributions . . ." (THIS JOURNAL, Vol. LXXIV, pp. 209-239), at p. 238, line 22, instead of the first variate read $\sqrt{n} \cdot (\bar{X} - A)/\sigma$, for, writing v_1 and v_2 for the variates in line 20, the appropriate orthogonal transformation is

$\frac{v_1\sqrt{n_1} + v_2\sqrt{n_2}}{\sqrt{(n_1 + n_2)}}, \frac{v_1\sqrt{n_2} - v_2\sqrt{n_1}}{\sqrt{(n_1 + n_2)}}$, which gives the correct new pair of variates.

STUDIES IN SEMIQUINONES.

PART I. p-PHENYLENE DIAMINE AND BENZIDINE DERIVATIVES.

By G. K. HUGHES and N. S. HUSH.

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The most recent theory of the structure of Wurster type dyes (oxidation products of p-phenylene diamines) is that of Michaelis and Granick (1943).

The amines from which these authors prepared their crystalline δ -salts¹ include 1:4-diaminobenzene, 1:4(bis)-methylaminobenzene, 1-amino,4-dimethylaminobenzene, 1-dimethylamino,4-methylaminobenzene and 1:4(bis)-dimethylaminobenzene.

The anions, used to precipitate the organic cations as salts, were perchlorate, iodide and bromide.

The main conclusions of Michaelis and Granick are as follows:

(1) In dilute solution Wurster salts are free resonance-stabilized semiquinone ions; at low temperatures and high concentrations they may polymerize, in which case there is an equilibrium between the monomeric and the polymeric forms.

(2) The solid δ -salts are either wholly in the s-form or wholly in the π -form.

(3) Polymerization will occur only when the parent diamine has at least one unsubstituted hydrogen atom on one of its amino groups.

(4) If all the amino hydrogen atoms are substituted, no dimeric bond can be established, and the compound remains a free radical even in the solid state.

(5) The polymerized molecule is a linear resonating structure in which the moieties involved in the exchange are diamine and diiminium ion (with a double positive charge). The two rings lie in the same plane and the four atoms attached to the central N atoms lie in a plane perpendicular to that of the benzene rings. The steric hindrance of alkyl groups weakens the bond (formed by the exchange of an electron pair between the two central N atoms) and makes the compound unstable.

¹The nomenclature, used in this paper for the solid salts, is an extension of that of Michaelis, Granick and Schubert (1940), and Michaelis and Granick (1943). The salt is named by reference to the diamine from which it is derived and the anion used to precipitate the organic cation. Four prefixes are employed:

δ -Salts are those which are on the oxidation level of semiquinones. In using this prefix no commitment is made as to whether the salt is a free radical or a polymer. δ -Salts may be subdivided into two classes:

(a) s-Salts are salts of monomeric free semiquinone ions.

(b) π -Salts are those in which the semiquinone ions are polymerised. In agreement with the above-mentioned authors, no distinction is made between dimers and higher polymers; the dimeric unit is convenient for illustrating the theory and is always referred to, but this does not exclude the possibility of the resonance extending over the entire crystal.

ω -Salts are the almost colourless hygroscopic salts on zero oxidation level obtained from some s- and π -salts on standing.

This paper contains experimental evidence which conflicts with statements (2), (3) and (4) and shows that (5) must be modified; alternative explanations of the facts brought forward by Michaelis and Granick are advanced.

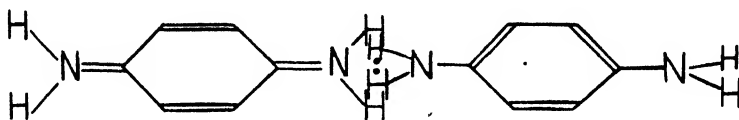


Fig. 1.—The axes of the two benzene rings are co-linear and the rings are co-planar. The central imino- and amino-H atoms lie at the vertices of a square perpendicular to the plane of the ring.

Before presenting these it may be pointed out that while the Michaelis-Granick theory of the dimeric resonance bond is consistent both with resonance theory and with experiment in the meriquinone field in so far as it postulates resonance between forms which possess a quinoid and a hydroquinoid part, the theory is inconsistent with experimental evidence adduced by these authors when it postulates that the moieties of each resonant state must have a linear coplanar arrangement.

This latter postulate requires that the atoms or groups attached to the central resonance-bonded nitrogen atoms are linked to a different nitrogen atom in each limiting state. While this is conceivable in the case of the δ -salts of 1:4-diaminobenzene, in which the atoms concerned are hydrogen, it cannot explain the formation of the dimeric bond in the δ -salts of 1:4-(bis)-methylaminobenzene, 1-amino:4-dimethylaminobenzene and 1-dimethylamino:4-methylaminobenzene, for this would require that in each case methyl groups were being exchanged between the central nitrogen atoms.

In modifying the theory so as to eliminate the postulation of interchange of the amino-substituents, there are two alternatives. The postulate of coplanarity may be abandoned, in which case the rings are perpendicular (Fig. 2). The abandonment of this postulate is consistent with resonance theory, for coplanarity of resonating moieties is demanded only when partial double bond character is imposed on a bond owing to resonance interchange.

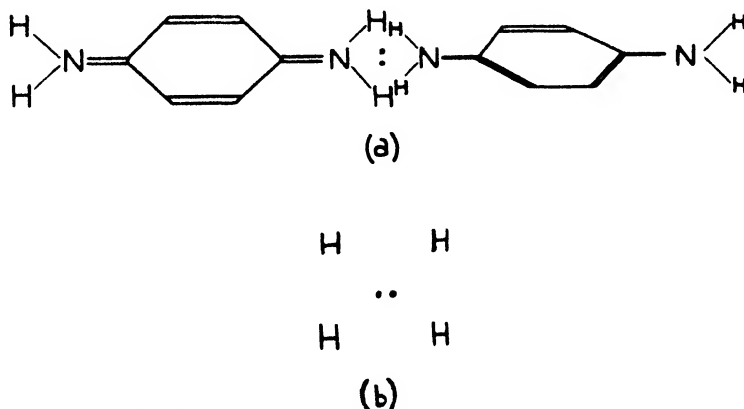


Fig. 2.—The axes of the two benzene rings are co-linear and the rings lie in mutually perpendicular planes. The imino-H atoms lie in the plane of the attached molecule; the amino-H atoms lie approximately in the plane of the Kekule ring. The four central H atoms lie approximately at the vertices of a square in a plane perpendicular to both rings.

Alternatively, the postulate of co-linearity of the benzene rings may be abandoned, in which case a limiting structure of the type shown in Fig. 3 would be expected.

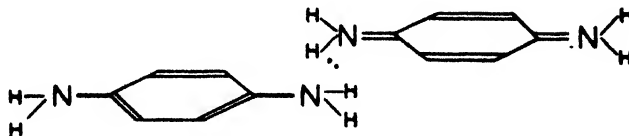


Fig. 3.—The axes of the two benzene rings are not co-linear, and the rings lie in parallel planes. The central H atoms lie approximately at the vertices of a square in a plane inclined to the rings.

RESULTS AND DISCUSSION.

1. δ -Salts of Fully N-substituted Diamines.

Michaelis and Granick obtained no "satisfactory" bromides or iodides of 1:4-(bis)-dimethylaminobenzene and Willstatter and Piccard (1908) also failed to obtain a reproducible bromide.

However, reasonably reproducible salts have now been obtained using these anions when certain factors were controlled, particularly the nature of the solvent.

Paramagnetic bromides and iodides of magnetic susceptibility close to that calculated for free radicals (monomeric semiquinone ions) with one unpaired electron, and also, under different conditions, salts with low susceptibility were obtained. These last-mentioned salts (γ -halides)² were obtained either by oxidation in methanol or aqueous methanol solution followed by precipitation with ether, or alternatively by oxidation in ether-methanol or dioxane solution. The γ -halides were brownish powders with a violet streak; they differed in appearance from the brilliant silky lustre of the paramagnetic salt.

Both types of salt altered rapidly (and irreversibly), on standing, to almost colourless compounds (ω -salts) of the same empirical formulae, but no longer giving the intense blue solution characteristic of Wurster's Blue³ when dissolved.

The relevant data for these salts are listed in Table I.

The oxidation levels, listed in Table 1, as measured by catalysed hydrogen uptake in Warburg manometers, indicate that both the paramagnetic and the γ -salts are on the first semiquinone level. The results suggest that separation of salts with low susceptibility is associated with a low dielectric constant of the precipitating medium.

The paramagnetic halides are identified as free radicals of 1:4-(bis)-dimethylaminobenzene. In order to account for the properties of the γ -salts, it will be necessary to assume one of the following: (a) That the γ -salt is a mixture of the s -form and the π -form. (b) That the γ -salt is a mixture of the s -form and the ω -form. (The hypothesis of incomplete bond formation, which has been advanced (Michaelis and Schubert, 1938) to account for the anomalous susceptibility of Kuhn and Ströbele's arabinoflavins (Kuhn and Ströbele, 1937), for example, is not considered here, as it is inconsistent with the all-or-none law for bond formation (Pauling, 1939).)

² Salts of anomalously low susceptibility are termed in this paper γ -salts.

³ Salts of the semiquinone ion derived from 1:4-(bis)-dimethylaminobenzene are called salts of Wurster's Blue.

TABLE 1.

δ-Salts of 1:4-(bis)-dimethylaminobenzene.

Salt.	Oxidation Level. (H ₂ uptake in μl/mg. at N.T.P.)		Solvent.	Magnetic Susceptibility. (χ _m × 10 ⁶ c.g.s.)			T° C.
	Calculated.	Observed.		Calculated.		Observed.	
				Radical.	Dimer.		
s-Bromide ..	52 0	43 0	10% MeOH (a)	+ 1133	- 154	+ 1040	16
γ-Bromide ..	52 0	46.0	MeOH, Et ₂ O (b) (ppd.)	„	„	+ 96	14
s-Iodide ..	31 0	21.0	10% MeOH	+ 1127	- 160	+ 1004	16
γ-Iodide ..	31 0	24 0	MeOH, Et ₂ O (ppd.)	„	„	+ 51	16
ω-Bromide ..	(0)	0	(In vacuo)	—	- 154	- 142	15
ω-Iodide ..	(0)	0	(In vacuo)	—	- 160	- 138	17
s-K ₂ Fe(CN) ₆ ..	30.2	25 0	10% MeOH	+ 1158	- 120	+ 1031	18
ω-K ₂ Fe(CN) ₆ ..	(0)	0	(In vacuo)	—	„	- 131	17

Notes.—(a) I.e., 90 volumes methyl alcohol and 10 volumes water.

(b) I.e., precipitated by ether from methyl alcohol solution.

Alternative (b), although unlikely, is listed as a possibility because of the rather large limit of error in the oxidation level determinations. However, the measurements were made immediately after preparation, and the rate of conversion to the ω-form was found to be too slow (even with the most unstable salts) to account for the low susceptibilities.

Alternative (a) is the more probable explanation of the anomalous susceptibilities. (This hypothesis was the alternative to that of partial bond formation originally advanced by Schwarzenbach and Michaelis (1938) to explain the low susceptibilities in the flavin series.)

Against this conclusion it might be claimed that the potentiometric examination of Wurster's Blue already published (Michaelis, 1931; Michaelis and Hill, 1933; Michaelis, Schubert and Granick, 1939) has failed to reveal any signs of dimerization in solution. This aspect of the problem will be discussed in a later paper; but it can be pointed out here that the published potentiometric work provides no conclusive evidence against the possibility of dimerization of the Wurster's Blue radical, since—

- (i) the potentiometric experiments published have been carried out in water or water-methanol, whilst the γ-salts have been obtained from either ether or dioxane solutions; and it is known that change of solvent has a marked influence on dimerization equilibria.
- (ii) The experiments on Wurster's Blue have been carried out at a dilution which has since been found to be unfavourable to dimer formation. (Michaelis and Schubert, 1938.)
- (iii) The parallel examination of the semiquinone ion of 1-amino:4-dimethylaminobenzene (Wurster's Red) (Michaelis, 1931) failed to reveal dimerization of the 1-amino:4-dimethylaminobenzene radical.

Included in Table 1 are data for the $K_3Fe(CN)_6$ salt of 1:4-(bis)-dimethylaminobenzene. (For remarks on the ferrocyanide series, see Section 2.) This salt is unstable, although immediately after preparation it exhibits the typical colour and lustre of the radical, it changes in a few days to the silvery-white ω -salt, with a χ_m close to the Pascal diamagnetic correction. This shows that paramagnetism of salts of the ferrocyanide series is not even in part due to the anion.

As another test of conclusions (2) and (3) of the Michaelis-Granick theory, δ -salts of 4:4'-(bis)-dimethylaminodiphenyl were isolated. The possibilities of resonance in the benzidine series are substantially the same as in the p-phenylene diamine series.

With the anions bromide and perchlorate, deep green powders were obtained on treatment with bromine, and these changed on standing in vacuo or in the air or on warming to a light yellow powder (presumed to be the ω -form). Methanol solutions of the green oxidation product do not change colour on cooling to $-40^\circ C.$, but, on warming to $50^\circ C.$ the colour reversibly changes to a light yellow; the process may be repeated many times. This looks similar to the typical dimerization phenomena of meriquinoid salts; however, the experiments of Lewis and Lipkin (1942) on photosensitized oxidation of 4:4'-(bis)-dimethylaminodiphenyl in rigid solvents indicate that the monomer of 4:4'-(bis)-dimethylaminodiphenyl is green, which suggests that the colour change is not due to dimerization. No explanation of this is offered. There is, however, the possibility that the amine is associated in the rigid solvent in Lewis' and Lipkin's experiments.

Complete analysis of the green bromide showed it to have the empirical formula $C_{16}H_{20}Br$; further, it was found that all the bromine present was ionizable, *i.e.*, there is no nuclear bromination.

In the ω -form the bromine was also ionizable.

Data for the bromide and perchlorate salts are given in Table 2.

TABLE 2.

δ -Salts of 4:4'-(bis)-dimethylaminodiphenyl.

Salt.	Oxidation Level. (H ₂ uptake in μl/mg. at N.T.P.)		Solvent.	Magnetic Susceptibility. (χ _m × 10 ⁶ c.g.s.)			T° C.
	Calculated.	Observed.		Calculated.		Observed.	
				Radical.	Dimer.		
π-Perchlorate ..	37.5	34.1	10% MeOH	+1135	-152	-166	16
			20% MeOH	"	"	-170	15
π-Bromide ..	35.3	37.0	10% MeOH	+1128	-154	-173	17
	35.3	34.0	CHCl ₃	+1135	"	-170	16
			20% MeOH	"	"	-168	16
ω-Perchlorate ..	(0)	0	(In vacuo)	—	(-152)	-153	16
ω-Bromide ..	(0)	0	(In vacuo)	—	(-154)	-155	14

These results show that the salts are wholly diamagnetic and that the green form is on the first semiquinone level. They are thus identified as π -salts of 4:4'-(bis)-dimethylaminodiphenyl; again it would seem that a dimer has been formed even when the amino groups of the parent amine are completely substituted.

2. δ -Salts of Partially N-substituted Diamines.

In order to test conclusion (3) of the Michaelis-Granick theory, attempts were made to prepare δ -salts with anions other than bromide, iodide and perchlorate. Iodates, chromates and benzoates could not be isolated, but a series of ferrocyanides was obtained by the addition of aqueous potassium ferricyanide to aqueous methanol solutions of the free amine (sometimes saturated with potassium ferrocyanide). For the salts to be described, the reaction can be represented as $A + K_3Fe(CN)_6 \rightarrow AK_3Fe(CN)_6$. For purposes of comparison the perchlorates were also prepared.

Data for these salts are given in Table 3.

TABLE 3.
(a) δ -Salts of 1-Amino-4-dimethylaminobenzene.

Salt.	Solvent.	Magnetic Susceptibility ($\chi_m \times 10^6$ c.g.s.).			T° C.
		Calculated.		Observed.	
		Radical.	Dimer.		
π -Perchlorate	10% MeOH	+1150	128	- 105	18
s-Ferrocyanide (a)	20% MeOH	+1173	- 96	+ 1098	20
π -Iodide	10% MeOH	+1141	- 146	- 120	16
π -Bromide	10% MeOH	+1148	- 130	- 130	18

(b) δ -Salts of 1:4-Methylaminobenzene.

π -Perchlorate . . .	10% MeOH	+1141	-128	-136	20
(s+w)-Ferrocyanide (b)	20% MeOH	+1182	-96	to +18	18
π -Iodide . . .	10% MeOH	+1141	-146	-115	16
π -Bromide . . .	10% MeOH	+1152	-130	-100	17

Note on Table 3.—a: This is the first paramagnetic solid salt of 1-amino-4-dimethylaminobenzene that has been described. A brief note by Pauling (1939) claims that in unpublished experiments by Pauling and Sturdivant a paramagnetic iodide of Wurster's Red was obtained. The formula given for the radical, however, is that of the salt of 1:4-(bis)-methylaminobenzene, which is not Wurster's Red.

We were unable to obtain anything but a diamagnetic iodide or bromide by oxidation of 1:4-(bis)-methylaminobenzene. Both salts are stable and the values of the magnetic susceptibility for the iodide and the bromide are in substantial agreement with the figures of Michaelis and Granick.

b: This salt had the usual semimetallic lustre of the paramagnetic salts, but changed very rapidly to the colourless (silvery) ω -form, which gives almost colourless solutions. It is evidently a very unstable radical.

The data for the perchlorates (Table 3) agree substantially with those published by Michaelis and Granick.

It is seen that the anion has a considerable influence on the state (σ - or π -) and stability of the precipitated salt. Whereas with the perchlorate a very stable free radical for the δ -salts of 4:4'-(bis)-methyaminobenzene and an unstable dimer for those of 1:4-(bis)-methyaminobenzene and 1-amino,4-dimethylaminobenzene are obtained, with the $K_3Fe(CN)_6$ anion a very stable radical for δ -salts of 1-amino,4-dimethylaminobenzene and an unstable radical for δ -salts of 4:4'-(bis)-dimethylaminodiphenyl and 1:4-(bis)-methyaminobenzene are obtained.

3. δ -Salts derived from 4:4'-diaminodiphenyl (benzidine).

Since the beginning of the century several workers have investigated the structure of the oxidation products of benzidine. In particular, Barzilovsky (1905) and Schlenk (1908) have shown that these oxidation products are meriquinoid salts and all analyse according to an empirical formula, A_nX , where A is the positive cation derived from benzidine and X is an anion of valency n.

The bromide, perchlorate and ferrocyanide δ -salts of benzidine have been prepared and the data for these salts are listed in Table 4.

TABLE 4.
 δ -Salts of 4:4'-Diaminodiphenyl.

Salt.	Oxidation Level.		Solvent.	Magnetic Susceptibility ($\chi_m \times 10^6$ c.g.s.)			T° C.
	Calculated.	Observed.		Calculated.		Observed.	
				Radical.	Dimer.		
π -Perchlorate ..	—	—	10% MeOH	+1086	—201	—116	16
π -Bromide ..	48.1 (a)	44.0	10% MeOH	+1079	—203	—123	17
Ferrocyanide ..	4.0 (b)	4.1	MeOH susp.	—	—485	+685	16
Ferrocyanide ..	4.0 (b)	3.8	H ₂ O susp.	—	—485	+1290	15

Notes.—(a) H₂ uptake in μ l/mg. at N.T.P., measured manometrically.

(b) Oxidation level determined by method of Schlenk (1908).

Note to Table 4.—Consideration of the results of photosensitized oxidation of benzidine and its derivatives (first observed by Noack (1925) and discussed by Weiss and Fishgold (1936)) and of the early work on analysis of the salts led J. Weiss (1938) to maintain that the meriquinoid salts, which had been thus far described, were all positive benzidine-ion free radicals. This does not appear to be the case.

If the ferrocyanide salts are indeed of the semiquinone type, the variation in magnetic properties of these δ -salts could be explained in the same manner as the similar variation in the δ -salts of the p-phenylene diamine series. It must also be noted that the highest Bohr magneton number calculated for the ferrocyanides from the observed mean moments is less than half the value calculated by means of the van Vleck formula and the Curie law for the molecule Bz_4X , with four unpaired electrons.

SUMMARY.

The above results show the following:

(a) Solid s -salts (on the first semiquinone oxidation level) may be obtained from all the amines studied with the possible exceptions of 4:4'-(bis)-dimethylaminodiphenyl and 4:4' diaminodiphenyl.

(b) Salts, which are mixtures of the semiquinone ion and the dimerized form, can be obtained by suitable selection of conditions.

(c) By variation of the anion it is possible to prepare either paramagnetic or almost diamagnetic δ -salts of 1:4-(bis)-methylaminobenzene, 1-amino, 4-dimethylaminobenzene, 1:4-(bis)-dimethylaminobenzene and possibly 4:4'-diaminodiphenyl (benzidine).

If the restrictions of the Michaelis-Granick theory, which lead to the postulation of interchange between the central nitrogen atoms of the dimer of groups attached to them during the resonance cycle, are removed and a structure such as that shown in Fig. 2 or in Fig. 3 substituted for these, then the structural criterion for dimer formation will be *simply* whether or not the steric strain is sufficient to counterbalance the increase in resonance energy gained by dimerization. And there is no reason to suppose that this will be the case with derivatives of completely N-methylated diamines.

Parts (b) and (c) may be re-stated as follows:

Salts, which are a mixture of the radical and of the dimer, will be isolated only from solutions in which an equilibrium exists between these two forms, as well as the totally reduced and totally oxidized forms. Where such an equilibrium exists, the ratio of s to π in the salt formed with a specified anion will depend upon (i) the semiquinone dimerization and dimeric formation constants governing the equilibrium, and (ii) the relative solubilities of the salts of s and π with the anion.

The consequences of this hypothesis relevant to (b) and (c) are:

I. For any specified anion the magnetic moment of the salt (taken as a measure of the ratio s/π) will vary if the solvent is changed and if the conditions of formation, which affect the values of the effective semiquinone, dimerization and dimeric formation constants (Michaelis and Schubert, 1938) are altered.

II. Variation of the anion will be expected to produce a change in susceptibility where other conditions are maintained constant owing to the fact that the solubility ratio S_s/S_π will vary for each anion. Confirmation is to be found by contrasting the halides with the $K_3Fe(CN)_6$ salt of 1-amino, 4-dimethylaminobenzene (Wurster's Red). The susceptibility of the halides is that of the dimer; of the ferrocyanide, that of the radical. Both types of salt are isolated from a deep blue solution, *i.e.*, from one which contains a large (if not predominant) proportion of dimer. It will be expected that in this case the s -ferrocyanide is less soluble than the π -ferrocyanide.

This hypothesis, if correct, might account for the numerous anomalously low susceptibilities cited in the literature, *e.g.*, for the arabinoflavins, and for Katz's dihydropyocyaninium and tetra-*p*-tolylhydrazinium perchlorates.

Finally, two further details of the Michaelis-Granick theory are open to question. Firstly, these authors, in their exposition of Pauling's all-or-none law, speak of the "assumption that no molecular collision resulting in chemical interaction can occur in the solid state" and deduce that "in the crystalline state only resonance, but no chemical reaction, occurs". The

all-or-none law, however, forbids only resonance between structures with different numbers of unpaired electrons, so inferences about the impossibility of a reaction cannot be drawn. In particular, the transition to the ω -form takes place in the solid state.

Secondly, from the fact that the rate of conversion of the π -form to the ω -form of a salt varies with (among other factors) the nature of the original amine, Michaelis and Granick conclude that the faster the rate of conversion, the weaker is the dimeric bond in the π -salt. This is untenable, as it involves a confusion of free energy with energy of activation.

EXPERIMENTAL.

Methods of Measurement.

Magnetic measurements were made by the Gouy method. All measurements were made at a current of 3 amperes, and the amount of material used for each determination was 0.4 gm. The weighing tube constants were determined by standardization with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The theoretical values for the magnetic susceptibilities of the δ -salts were calculated by means of the equation of Van Vleck (1932) and the unmodified Curie law. The structural, atomic and ionic diamagnetic contributions to molar susceptibilities values are based on the modified Pascal constants (c.f. Selwood, 1943) and those of Trew (1941). The values calculated for the theoretical diamagnetic susceptibility differ from those of Michaelis and Granick, presumably owing to the use of different values for the anionic diamagnetic susceptibility.

Oxidation level determinations were carried out by catalytic micro-reduction, using the Warburg constant volume manometers. The most efficient procedure was found to be the following: In each cup was placed a weighed amount (2-7 mg.) of the substance, a measured volume of solvent added, and a measured amount of catalyst placed in the side-arm. The solutions were first equilibrated and then the catalyst was mixed in. The usual manometric technique was employed; it was found that several blank experiments were required for each set.

Of catalysts employed, a colloidal palladium sol containing 1 gm. Pd per litre (prepared by the reduction of palladous chloride in the presence of gelatin) was the most efficient.

Raney nickel and colloidal Pd and Pt prepared by the Bredig method were either less active or gave unreproducible results.

The oxidation level was in one case (ferrocyanide salt of 4:4'-diaminodiphenyl) determined by macro-reduction using stannous chloride, after the method of Schlenk (1908).

PREPARATIONS.

δ -Salts of 1:4-(bis)-Dimethylaminobenzene.

Perchlorate: This was prepared from the amine hydrochloride according to the method of Michaelis and Granick (1943), and also from the free amine. The amount of bromine added (corresponding to 0.7 equiv.) was 50 mls. 0.025 N bromine per 2 gms. dihydrochloride, or per 1.4 gm. amine. The product was purified before measurements were taken by shaking with distilled water and filtering several times.

s-Bromide: A solution of 0.8 gm. of the free amine in 90% methanol was cooled to -10°C ., stirred slowly, and 0.7 equiv. bromine in 6 mls. methanol added dropwise. Stirring was continued for several minutes after completion of bromine addition; the solution was then filtered through sintered glass. The product was washed first sparingly with distilled water, then with methanol; finally it was washed abundantly with dry ether. The product consisted of brown needles with metallic lustre, which gave an indigo blue streak. Found: Br, 29.8%. Calculated for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{Br}$: Br, 32.6%.

γ -Bromide: The oxidation was carried out with the same amount of bromine as for the *s*-bromide. The salt was either (a) precipitated from an 80% ether-methanol solvent or (b) precipitated by ether from an excess methanol solution. In each case the salt which separated possessed a low moment. The analysis recorded is for salts prepared by method (a). Found: N, 11.10; Br, 31.82%. Calculated for $C_{10}H_{16}N_2Br$: N, 11.06; Br, 32.60%.

***s*-Iodide:** A 90% aqueous methanol solution of the free amine was treated with 0.7 equivalents of iodine in methanol solution at 0°C. The salt separated in long needles with a brilliant sub-metallic lustre. The iodide was more stable than the *s*-bromide. It was filtered off and purified as in the preceding methods. Found: I, 42.86%. Calculated for $C_{10}H_{16}N_2I$: I, 43.60%.

γ -Iodide: This salt was obtained by oxidation of the free amine with 0.7 equiv. iodine. As with the γ -bromide, two methods were followed: (a) the oxidation was carried out in 80% ether-methanol, from which the salt separated, or (b) the salt was precipitated from an excess methanol solution by ether. The product was purified as before, and did not possess the needle form or the lustre of the corresponding *s*-salt. The analysis recorded is that of the salt prepared by method (b). Found: C, 41.60; H, 5.60; I, 42.70%. Calculated for $C_{10}H_{16}N_2I$: C, 41.24; H, 5.53; I, 43.60%.

Ferrocyanide: This was prepared from the free amine in aqueous methanol solution. The solution was cooled to 0°C. and 0.7 equivalents aqueous potassium ferrocyanide (in 1 ml.) pipetted in slowly with stirring. The salt, which separated from the intensely blue solution exhibited the needle form, brown colour, sub-metallic lustre and blue streak characteristic of paramagnetic Wurster's Blue salts. The salt was unstable and changed to the light green hygroscopic ω -form in a few days. Found: N, 22.63%. Calculated for $C_{16}H_{16}N_8FeK_3$: N, 22.70%. The ω -form of this salt was analysed for nitrogen, but the figure is not thought to be accurate owing to the extremely hygroscopic nature of the salt. Found: N, 21.50%. Calculated for $C_{16}H_{16}N_8FeK_3$: N, 22.7%.

δ -Salts of 1-Amino,4-dimethylaminobenzene.

Ferrocyanide: An aqueous methanol (10% MeOH) solution of the free amine was cooled to -5°C., and 0.7 equiv. potassium ferricyanide dissolved in the minimum amount of distilled water, was run in from a pipette with constant stirring. The green salt, which separated from an intensely blue solution, was filtered over sintered glass, and washed sparingly with methanol, distilled water, and dry ether. The dry salt exhibited a brilliant sub-metallic lustre under the microscope, gave deep red dilute solutions and deep blue concentrated solutions. The salt was stable for months. Found: C, 35.83; H, 2.61; N, 26.03%. Calculated for $C_{11}H_{11}N_8FeK_3$: C, 36.12; H, 2.60; N, 24.08%.

The bromide, iodide and perchlorate of this amine were prepared both (1) from the hydrochlorides, after the method described by Michaelis and Granick (1943), and (2) from the free amine. No difference was observed between salts prepared by the two methods.

δ -Salts of 4,4'-(bis)-Dimethylaminodiphenyl.

Perchlorate: To a solution of 100 mls. 90% aq. methanol containing 10 gms. sodium perchlorate, 0.4 gm. 4,4'-(bis)-dimethylaminodiphenyl dihydrochloride were added. The clear solution was filtered and cooled to -5°C.; then 9.6 mls. 0.103 N aq. bromine were added dropwise with vigorous stirring. The precipitate was filtered and formed a deep blue filter cake, which dried to a deep green. It was washed abundantly with distilled water, methanol and dry ether. Yield: 0.3 gm. Found: N, 8.18%. Calculated for $C_{18}H_{20}N_2ClO_4$: N, 8.25%.

Bromide: To a solution of 810 mls. methanol was added 2.92 gms. of the dihydrochloride, and 120 mls. of an aq. solution of sodium bromide (containing 30 gms. NaBr) stirred in. After cooling to -5°C., 70 mls. 0.095 N aq. bromine were added dropwise

with stirring. The bluish precipitate was collected and treated as above. The filtrate was straw yellow. Yield: 2.5 gms. Found: N, 8.75; Br, 24.96%. Calculated for $C_{10}H_{20}N_2Br$: N, 8.65; Br, 24.68%.

Ionizable bromine analyses were carried out on both the green bromide and the ω -bromide. 0.15 gm. samples were used in each case.

	NaOH Neutralization Observed.	NaOH Neutralization Calculated (for 1 equ. bromide/320 gms.).
Bromide	0.0186 gm.	0.0188 gm.
ω -Bromide	0.0181 gm.	0.0188 gm.

8-Salts of 4:4-Diaminodiphenyl (Benzidine).

Bromide: To a solution of sodium bromide (50 gms.) in 1 litre methanol was added benzidine (2 gms.); this was stirred until completely dissolved and the solution filtered. The filtrate was cooled to $-10^\circ\text{C}.$, and 72 mls. of 0.106 N aq. bromine added dropwise with constant stirring. The blue suspension was filtered, washed abundantly with distilled water, methanol and dry ether. The product was a deep indigo blue powder, apparently amorphous. Yield: 1.6 gms. (The temperature of the preparation was varied and the magnetic susceptibility of the product was not altered until a temperature of about $50^\circ\text{C}.$ was used.) Found: C, 54.48; H, 4.78; N, 10.10; Br, 29.31%. Calculated for $C_{12}H_{12}N_2Br$: C, 54.56; H, 4.58; N, 10.60; Br, 30.26%.

Perchlorate: An exactly similar method was used, with sodium perchlorate in place of sodium bromide. Yield: 1.8 gms.

Ferrocyanide: (1) 3 gms. finely powdered benzidine were suspended in 330 mls. distilled water and vigorously stirred. A solution of 3.6 gms. potassium ferricyanide in 18 mls. water was added dropwise to the suspension over a period of half an hour. The stirring was continued for a further half-hour, after which the blue suspension was filtered through sintered glass. The filter cake was washed abundantly with cold distilled water, then with absolute ethanol until the bromine test showed all unchanged benzidine had been removed; finally it was washed with dry ether.

(2) The same method was followed except for the use of methanol or methanol-water mixtures for the suspending liquid.

(3) Benzidine dihydrochloride in aqueous solution was used.

Found: C, 65.14; H, 5.19 (using preparation from method (1)); N, 21.20% (from method (2)); and N, 21.50% (from method (3)). Calculated for $C_{14}H_{18}N_4FeK_2$: C, 68.34; H, 5.09; N, 21.11%.

The filtrate from the preparation of bromide was almost colourless; that from the ferrocyanides was light green, darkening markedly on standing.

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DETERMINATION OF MAXIMUM INHERENT MOISTURE IN COAL BY CONTROLLED VAPORISATION OF ADHERENT MOISTURE.

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INTRODUCTION.

The rôle of inherent moisture in coal, its relations to micelle structure and rank, and difficulties in determination of its maximum values have been reviewed in recent papers by Dunningham (1943), Bangham (1943) and King and Wilkins (1943).

The total moisture content of freshly-mined coal consists of *inherent moisture* held by capillary condensation or adsorption on the internal surface (or intermicelle spaces) of the coal substance, as well as *adherent moisture* which may be present on the external surface of the coal and in cracks and internal cavities too large to be considered part of the structure of the coal substance.*

Inherent moisture is distinct from adherent moisture in so much that its vapour pressure is lowered by the small diameter of the spaces in which it is adsorbed. *Maximum inherent moisture* is that which coal contains when all capillary spaces are filled with adsorbed moisture but no adherent moisture is present. In its original condition in the seam, coal usually contains its maximum inherent moisture content together with a variable quantity of adherent moisture which is really ground-water lying, or circulating, in the seam and associated strata. In well-drained strata outcropping on hillsides there may be very little adherent moisture in the seam, and in some cases it appears that the total moisture content may be less than the maximum inherent value.

When freshly mined, coal contains approximately the same amount of moisture as in the seam. When delivered to the consumer, the moisture may be much lower if the coal has been exposed to dry air which removes adherent moisture and part of the inherent moisture. If the coal has been washed in preparation for marketing, or exposed to rain during transport and storage, adherent moisture may have been added, giving a total moisture content higher than the original value.

The total moisture content of coal, as mined or at any subsequent stage, is readily determined by drying a representative sample at 105° C. in dry nitrogen. Moisture contents obtained in this way are required for industrial purposes, but they are of little value in scientific work when the fundamental properties of coal are to be compared or studied in relation to the structure of the coal substance. Moisture contents on the "air-dried" basis have been used in the

* The terms *adherent* and *inherent* are used in this paper to describe those portions of the total moisture content possessing normal and sub-normal vapour pressure respectively. In some brown coals, which have suffered but little compression and in which cleat has not developed, a considerable portion of the natural bed-moisture may be contained in openings too large to lower the vapour pressure of water, but which form an essential part of the coal structure, as pointed out by Dr. A. B. Edwards and Mr. J. R. Bainbridge, Melbourne University (private correspondence).

past for scientific purposes, but they are unsatisfactory as the amount of inherent moisture varies with relative humidity of the atmosphere in which the coal is dried. Results obtained by drying coal at constant humidity have also been used, but they are of no true value as they only indicate the amount of moisture held in capillaries of radii equal to, or smaller than, those capable of retaining water at the particular humidity employed.

For scientific work, including classification of different coals, results of true value are those based on maximum inherent moisture content. To obtain this it is necessary to make sure that all capillary spaces are completely filled with adsorbed water. This condition exists in coal sampled at a fresh damp face in underground workings but adherent moisture, also present, gives a total moisture content in excess of the maximum inherent value. When the fresh working face is not obviously damp, very little adherent moisture is present and unavoidable drying during crushing, sieving and handling in the laboratory may remove part of the inherent moisture, resulting in a content lower than the maximum inherent value. To avoid this, and to ensure that maximum inherent moisture is present, it is usually necessary to add water to the coal when sampled and to keep it wet during subsequent handling. If a little inherent moisture is lost by air-drying, the coal can be resaturated by immersing in water, or by standing in saturated atmosphere, for a prolonged period. While standing in saturated atmosphere the capillaries slowly fill with inherent moisture, and adherent moisture condenses and accumulates on the coal and in cracks.

It follows that determination of maximum inherent moisture depends on complete removal of adherent moisture from saturated coal without removing any inherent moisture from the coal substance, or on complete filling of capillaries with inherent moisture without allowing adherent moisture to collect on the coal. Once this is accomplished, maximum inherent moisture can be determined merely by drying the coal at 105° C. in dry nitrogen.

PREVIOUS METHODS USED IN DETERMINATION OF MAXIMUM INHERENT MOISTURE.

Methods previously available for determination of maximum inherent moisture are as follows (see also Dunningham, 1943) :

1. By plotting the adsorption curve for the coal up to the equilibrium moisture content at about 90% relative vapour pressure, and then extrapolating to 100%. This is unsatisfactory owing to the large degree of uncertainty regarding the form and position of the curves where they approach 100% saturation.

2. By exposing partially air-dried coal to saturated atmosphere until adsorption is complete, and then determining the moisture content. This method usually gives results which are too high and which cannot be satisfactorily reproduced, as adsorption is slow and adherent moisture commences to accumulate before the process is complete and continues until droplets of water can be seen on the coal.

3. By exposing wet coal (sample with excess adherent moisture) to unsaturated atmosphere until all adherent moisture is removed by evaporation. This is unsatisfactory, as complete removal of adherent moisture from cracks and inner cavities cannot be judged from the appearance of the coal, and it is probable that loss of inherent moisture commences before all the adherent moisture is removed.

4. The United States Bureau of Mines, Pittsburgh Experimental Station (1945), recently described a method for "Determination of Coal Surface Moisture" (i.e. adherent moisture) by placing a weighed quantity of wet coal in alcohol for a short (standardized) period of time then rapidly filtering off the

alcohol and determining the amount of water dissolved by change in specific gravity. This method was primarily designed for rapid determination of adherent moisture in coal for by-product coke ovens; in connection with bulk density and angle of repose of crushed coal; and as a routine check on efficiency of dewatering in coal washeries. It could be used for determination of maximum inherent moisture by first determining total moisture in the wet coal, and then adherent moisture removed by solution in alcohol—the difference between the two being the maximum inherent moisture. The results, however, would be relative, depending on length of time the coal remained in the alcohol, as inherent moisture is also removed from coal by solution in alcohol (Dulhunty, 1946). Furthermore, extraction time would have to be varied for coals of different rank and results may not be comparable.

5. A method devised by Dunningham (1943) in which adherent moisture is removed from wet coal by adsorption in blotting paper. The wet coal is shaken in a bottle lined with dry blotting paper, then transferred to another bottle, and the treatment repeated several times until the blotting paper remains dry, after which inherent moisture is determined by drying at 105° C. The method is standardised by using a given quantity of wet coal, crushed to a certain size, and by shaking for definite periods in bottles of given capacity for a certain number of times.

This is a simple, rapid and reliable method giving results which can be reproduced satisfactorily. It is suitable for industrial purposes and can be used in scientific work as demonstrated by Dunningham's results in the study of inherent moisture in coal. It would appear, however, that the blotting paper method has certain limitations. The results are relative rather than absolute as the amount of drying is standardised at that which appears to remove all adherent moisture. Short time of contact with dry blotting paper removes adherent moisture from the outer surface of coal particles, but not necessarily from all cracks and cavities, larger than capillaries, situated within the coal. Sufficient drying to remove all adherent moisture would possibly result in removal of some inherent moisture. The present writer found that coals of about the same rank and type can be satisfactorily compared by the blotting paper method, but different amounts of drying must be adopted for coals varying widely in rank and texture. Medium to high rank coals with compact texture require far less drying than low rank materials such as peat and brown coal of spongy, or fibrous, nature containing an abundance of internal cavities much larger than capillaries in the coal substance. It follows that results obtained for coals of different rank, requiring different amounts of drying, cannot be considered strictly comparable.

CONTROLLED VAPORISATION OF ADHERENT MOISTURE.

General Principles.

This method was developed with the object of obtaining results approximating to absolute values by a process which could be used, without variation in technique, for determination of maximum inherent moisture in coals of all rank and texture from peat to anthracite.

The method takes advantage of the fact that vapour pressure of inherent, or capillary-held, moisture is sub-normal, whilst that of adherent, or free, moisture is normal. It is based on the general principle that if wet coal is maintained at a constant temperature in an atmosphere of water vapour, or saturated air and water vapour, under a pressure which will just vaporise water at that temperature, adherent moisture with normal vapour pressure will pass to vapour, but inherent moisture with sub-normal vapour pressure will remain in the coal and can be determined by drying at 105° C. in the usual manner.

This principle offers the following advantages in determination of maximum inherent moisture. (i) Separation of adherent and inherent moistures depends on the difference in vapour pressure of the two, and the amount of moisture remaining in the coal, to be determined as maximum inherent moisture, is directly related to the total volume of capillary spaces capable of lowering the vapour pressure of water. It follows that results approximate to absolute values, and that they can be used in comparing moisture properties of coals of all rank and texture and for studying relations to physical and chemical rank-variation. (ii) The vaporisation process can be continued indefinitely until all adherent moisture is removed, without loss of inherent moisture as this is in contact with water vapour, or saturated air and water vapour, at a pressure higher than its vapour pressure. (iii) Adherent moisture is completely removed from all cracks and inner cavities as well as from the outer surfaces of coal particles. (iv) Adherent moisture is vaporised relatively quickly and a definite end-point is reached after which no more water is removed from the coal. This was established by plotting curves for moisture content at intervals during, and after, removal of adherent moisture. The process of vaporisation requires from six to eight hours, but apparatus can be designed to treat any desired number of coal samples simultaneously, enabling a large number of determinations to be carried out in a relatively short time. (v) The process can be carried out at any temperature from $100^{\circ}\text{C}.$ to room temperature. The pressure required to cause vaporisation varies with the temperature employed. Results obtained by determinations on duplicate samples at different temperatures agree very closely. It is desirable to adopt a relatively low temperature as prolonged heating in the vicinity of $100^{\circ}\text{C}.$ may cause physical changes in the micelle structure of some low rank coals, resulting in a reduction of internal surface and maximum inherent moisture. The most satisfactory temperature is one a little above the maximum temperature likely to be encountered in the laboratory, as it simplifies constant temperature equipment, enables the use of rubber fittings in the apparatus, and the coal is not heated appreciably.

Apparatus.

Apparatus suitable for controlled vaporisation of adherent moisture is illustrated diagrammatically in Figure 1. It consists of a glass tank or water-bath fitted with a mechanical stirrer and suitable equipment for maintaining constant temperature ($\pm 0.01^{\circ}\text{C}.$) at about $30^{\circ}\text{C}.$ A Beckmann thermometer is used for recording temperature. That part of the apparatus referred to as the pressure distributor carries a number of coal-tubes and is wholly immersed in the water-bath. It is connected by means of glass and rubber tubes to a saturated-air inlet valve, manometer and reduced-pressure control valve.

A pump is required, capable of reducing pressure to at least 5 mm. of Hg lower than the vapour pressure of water at the temperature of the water-bath. The pump is connected to the pressure control valve, which may be a manually operated needle valve, or an automatic control valve, by means of which any desired pressure can be maintained in the distributor and coal-tubes. The manometer connected to the distributor should be suitable for reading pressures accurately to 0.1 mm. of Hg. The saturated-air inlet valve is a small needle valve by means of which a very slow stream of air is allowed to enter the distributor under reduced pressure.

The distributor consists of a glass cylinder ($3\frac{1}{2} \times 1\frac{1}{4}$ in.) closed at both ends by rubber stoppers and divided into upper and lower compartments by a rubber partition. Ten coal drying-tubes ($3 \times \frac{1}{2}$ in.) fitted with rubber stoppers are attached to ten copper tubes ($1\frac{1}{4} \times \frac{1}{8}$ in.) which pass up through the base of the distributor into the lower compartment. The lower compartment communicates with the upper by means of a glass tube ($\frac{3}{32}$ in.) which passes up through the

rubber partition and extends to a position near the top of the upper compartment. The saturated-air inlet tube ($\frac{1}{8}$ in.) passes down through the top of the distributor to within $\frac{1}{8}$ in. of the base of the upper compartment. The tube ($\frac{1}{8}$ in.) leading to the pressure control valve passes into the top of the upper compartment. The tube ($\frac{1}{8}$ in.) from the manometer passes down through the top of the distributor, and the rubber partition, into the lower compartment.

When the apparatus is in operation, the upper compartment of the distributor is half filled with water. Air passing through the inlet valve is saturated at room temperature and pressure by bubbling through water before entering the valve. On entering the distributor it bubbles up through the water in the upper compartment and becomes saturated at the temperature and pressure maintained in the apparatus and coal-tubes. The slow stream of air helps considerably in maintaining constant reduced pressure in the system—particularly if a manually operated pressure control valve is used. Water vapour coming from the wet coal in the tubes passes into the lower compartment of the distributor, from which it displaces most of the air and then passes into the upper compartment, to be drawn off with saturated air through the pressure control valve. Small fluctuations in temperature or pressure may cause vapour and air to pass back into the lower compartment or even into the coal tubes. Any air which passes back in this way is saturated at the temperature and pressure in the coal tubes, and it cannot cause evaporation of inherent moisture.

Method.

Granular coal ($\frac{1}{8}$ to $\frac{1}{32}$ in.) is required for the determination. The coal must be thoroughly saturated with water to ensure that all capillary spaces are filled. If results are to correspond to maximum inherent moisture, as in the original seam-condition, fully air-dried coal should not be resaturated and used for the determination as irreversible changes in physical structure are likely to occur when coal is allowed to reach equilibrium moisture content at relative humidities lower than about 85%. Slightly air-dried coal, in which moisture has not fallen below the equilibrium content at about 90%, can be resaturated by immersing in water for at least seven days. The most satisfactory material is that to which water has been added immediately after sampling at a fresh face in underground workings and kept wet during subsequent handling in the laboratory. When prepared for moisture determination, the granular sample should contain a sufficient excess of adherent moisture to wet the inner surface of the coal tube, when filled, and produce small drops of water at points of contact between the coal grains and the glass. The drops appear as small dark spots on the wall of the tube owing to reflection effects at the curved surface of the glass.

The coal tubes, containing wet samples, are attached to the copper tubes on the distributor and the upper compartment is half filled with water. The distributor and coal tubes are then placed in the water-bath and connections are made to manometer, air inlet valve, and pressure control valve.

As a preliminary to the actual drying or vaporisation process, it is necessary at this stage to determine the "equilibrium pressure" at which neither vaporisation nor condensation of water occurs in the coal tubes at the particular temperature setting adopted on the Beckmann thermometer, as vaporisation is carried out at a pressure 0.3 to 0.4 mm. of Hg lower than the equilibrium pressure. This determination need not be made in subsequent dryings carried out at the same temperature if the mercury setting in the Beckmann is not disturbed.

To determine the equilibrium pressure, the water-bath is brought to the temperature selected on the Beckmann in the vicinity of 30° C. When temperature is steady ($\pm 0.01^\circ$ C.), the pressure control valve, connected to the pump, is opened and pressure in the distributor is reduced to within about 10 mm. of

the theoretical vapour pressure of water at the temperature of the water-bath and the air inlet valve is opened so as to allow a slow stream of air (about 40 bubbles per minute through the water in the distributor) to enter the system. Pressure is then reduced very slowly until adherent moisture just commences to vaporise as indicated by disappearance of excess moisture from the inner surfaces of the coal tubes, and slow reduction in size and number of the dark spots of water at points of contact between coal grains and the glass. This pressure

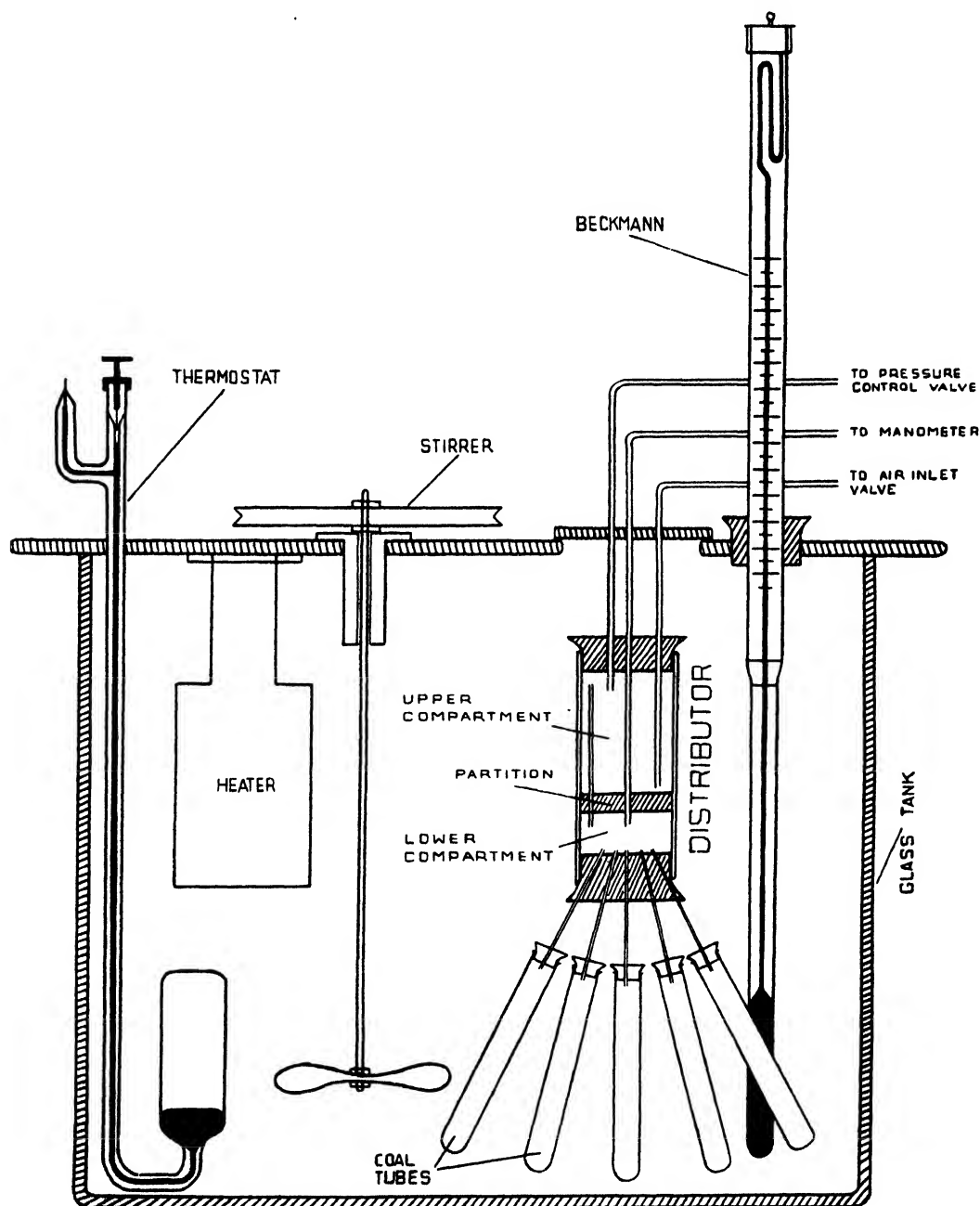


Fig. 1. Apparatus used for Vaporisation of Adherent Moisture.
(Five of the ten coal tubes are shown in diagram.)

is maintained (± 0.1 mm. indicated on the manometer) for about 20 minutes, after which time sufficient adherent moisture has vaporised to replace most of the air from the coal tubes and the lower compartment of the distributor. Pressure is then increased slowly until vaporisation ceases and condensation just commences as indicated by the appearance of dew on the inner surfaces of the coal tubes and a slight increase in size and number of the dark spots of water. Pressure is then reduced until vaporisation just commences again. After repeating this operation several times it is possible to determine the equilibrium pressure at which neither vaporisation or condensation occurs.

Having made the foregoing determination, vaporisation of adherent moisture is then carried out by reducing pressure to a manometer reading corresponding to 0.3 mm. to 0.4 mm. below the equilibrium pressure. This pressure is maintained until all traces of visible adherent moisture have disappeared from the coal tubes, which may require from one to four hours, depending on the amount of excess adherent moisture present in the first place. The process is continued for about three hours after removal of visible moisture to ensure vaporisation of all adherent moisture from cracks and inner cavities in the coal. Finally, pressure is increased by closing the pressure control valve, disconnecting the pump, attaching a water-bubbler, and allowing the distributor and coal tubes to fill with saturated air through the control valve. If removal of adherent moisture is not complete, dark spots of water will reappear when pressure is increased, and the process must be continued for an additional period.

When vaporisation of adherent moisture is complete, the coal tubes are removed from the distributor and the granular samples are transferred to glass-stoppered weighing bottles, previously weighed after filling with dry nitrogen at 105°C . This must be carried out without allowing the coal to come into contact with laboratory air which causes loss of inherent moisture by evaporation. It can be conveniently accomplished by using weighing bottles with necks of about the same diameter as the coal tubes. Each coal tube is disconnected from the distributor by withdrawing from the copper tube. The glass stopper is then removed from the weighing bottle as the rubber stopper is taken out of the tube, which is immediately placed against the neck of the bottle and inverted to run the coal down into the bottle. The tube is then removed as the glass stopper is replaced, and the bottle is weighed with the coal. (The transference of coal from tube to bottle need not be quantitative, as percentage of inherent moisture is determined in the coal actually transferred. Thus small particles of coal adhering to the inner surface of the tube may be neglected.) After weighing, the stoppers are removed from the weighing bottles, which are placed in an oven heated at 107° to 108°C . and a stream of dry nitrogen is introduced into each by means of a tube passing down through the neck to a position just above the surface of the coal. Oven drying by this method can be continued without danger of oxidation until the weight of dry coal is constant. Maximum inherent moisture is then calculated from loss of weight on oven drying, and expressed as a percentage of the weight of dry coal remaining in the weighing bottle.

Results.

At the equilibrium pressure, atmosphere in contact with the coal is approximately saturated. The pressure adopted for the determination (0.3 mm. to 0.4 mm. lower than the equilibrium pressure) was found in practice to be the pressure which would just cause vaporisation of adherent moisture at about 30°C . This means that the results correspond to equilibrium moisture contents at about 99% saturation. It does not appear possible to obtain results at full saturation, as adherent moisture is not removed and, theoretically, under such conditions inherent moisture would be infinitely great if sorption curves are

truly asymptotic to the 100% saturation line. The results, however, are believed to represent a close approximation to moisture content at full saturation which, for practical purposes, may be regarded as the conditions under which all capillaries forming part of the structure of the coal substance are completely filled with adsorbed water.

Variation of inherent moisture with pressure, under the conditions of determination, depends on the form of the sorption curves which probably vary considerably for different coals in the vicinity of 99% saturation. This factor influences the amount of error due to small fluctuations in temperature and pressure. Accurate data have not yet been obtained for pressure sorption relations above about 95% saturation, but it is hoped that this may form the subject of further investigation.

It follows that reproducibility of results depends on the form of the sorption curves, efficiency with which constant temperature and pressure are maintained during the vaporisation process, and accuracy with which moisture is determined by oven drying in the final stage. Also, as pointed out by Dr. D. H. Bangham (private correspondence), difficulty in avoiding small temperature gradients in the system, and the influence of the "hydrostatic level on pressure", may introduce error owing to the extreme experimental difficulty in exposing a macroscopic object to an atmosphere of uniform saturation.

Results in triplicate for a series of nine coals representing a wide range in rank and moisture content are given in Table I. The majority of coals give results which can be reproduced quite satisfactorily. Variations between duplicate determinations usually amount to less than 1.0% when expressed as maximum percentage deviation from the mean of the results, as illustrated by samples 1, 2, 3, 4, 6 and 8 in the table. With some coals it is more difficult to obtain close agreement between duplicate results, and percentage deviation may be somewhat higher, as in the case of samples 5, 7 and 9, which were included in the table to illustrate this feature. Such variation may be related to the form of the sorption curves where they approach a relative vapour pressure of 100%. In all cases, however, the actual variations between duplicate moisture values are relatively small compared with the total moisture contents and the large differences in moisture for coals of different rank.

TABLE I.
Reproducibility of Maximum Inherent Moisture Determinations.

No.	Coal Sample. Locality.	Rank.	Carbon A.F.D. Basis.	Triplicate Results.			Mean Value.	Varia- tion.	Max. % Deviation from Mean.
				Max 1	Inher. 2	Moist. 3			
1	Yallourn, Vic. . .	Brown coal.	68.4	80.20	80.70	81.60	80.83	1.40	0.95
2	Leigh Ck., Sth. Aust.	Brown coal.	71.9	54.70	54.30	54.50	54.50	0.40	0.33
3	Leigh Ck., Sth. Aust.	Sub-bitumen.	74.5	46.85	46.75	46.30	46.63	0.55	0.71
4	Collie, West. Aust. . .	Sub-bitumen.	74.8	20.20	20.40	20.15	20.25	0.25	0.74
5	Blair Athol, Q'land	Low - rank bitumen.	79.2	15.45	16.30	16.31	16.02	0.86	3.51
6	Wonthaggi, Vic. . .	Med. bitumen.	82.06	10.79	10.89	10.85	10.84	0.10	0.46
7	Borehold Seam, N.S.W.	Med. bitumen.	81.3	5.22	5.25	5.14	5.20	0.11	1.15
8	Greta Seam, N.S.W.	Med. bitumen.	80.8	3.06	3.07	3.02	3.05	0.05	0.98
9	Bulll Seam, N.S.W.	High - rank bitumen	90.0	1.76	1.70	1.77	1.74	0.07	2.31

From the results in Table I it does not appear as though there is any close relationship between the amount of variation in actual values for duplicate results and the magnitude of the moisture content. Samples 5, 4 and 2, containing 16.02%, 20.25% and 54.50% of moisture, gave variations of 0.86,

0.25 and 0.40 respectively. There is, however, a general tendency for coals with highest moisture to give the greatest variation, and those of lowest moisture to give the smallest variation, as seen in the fact that samples 1, 2 and 3 with over 40% moisture gave variations of 0.4 to 1.4, while samples 7, 8 and 9 with less than 6% moisture gave variations of 0.11 to 0.05.

Improvements or modifications to the apparatus and method may give results which can be repeated with less variation, but the degree of reproducibility already attained is as satisfactory as in methods previously available for determination of maximum inherent moisture. In addition, the results are believed to approximate to absolute values for coals of all rank and texture, and they may be used to advantage in comparing moisture properties of different kinds of coal, or in studying relations between maximum inherent moisture and physical and chemical rank variation.

The controlled vaporisation method—designed primarily for scientific research on fundamental properties of coal—is somewhat complicated and requires specialised apparatus. For this reason it may not be suitable for routine moisture determinations in industrial work where a simple rapid method is required to deal with large numbers of coal samples of about the same rank and type, but in this connection it may provide a means of standardising the amount, or time, of drying in the more simple methods so as to obtain results approaching true or absolute values.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge the assistance of Dr. D. H. Bangham (B.C.U.R.A., London), who kindly read the manuscript and offered valuable suggestions regarding theoretical consideration of results; helpful discussion with Dr. T. Iredale (Department of Chemistry, University of Sydney) during experimental work and preparation of results for publication; the assistance of Miss N. Hinder, B.Sc., in laboratory work.

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A MAGNETIC SURVEY IN THE VICINITY OF THE VOLCANIC NECK AT DUNDAS, N.S.W.

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'With Plate II and six Text-figures.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The Dundas volcanic neck is situated in the Parish of Field of Mars, County of Cumberland, about three miles to the north-east of Parramatta and about twelve miles north of west from Sydney. The position is shown on the Locality Plan, Fig. 1. The material of which it is composed has been

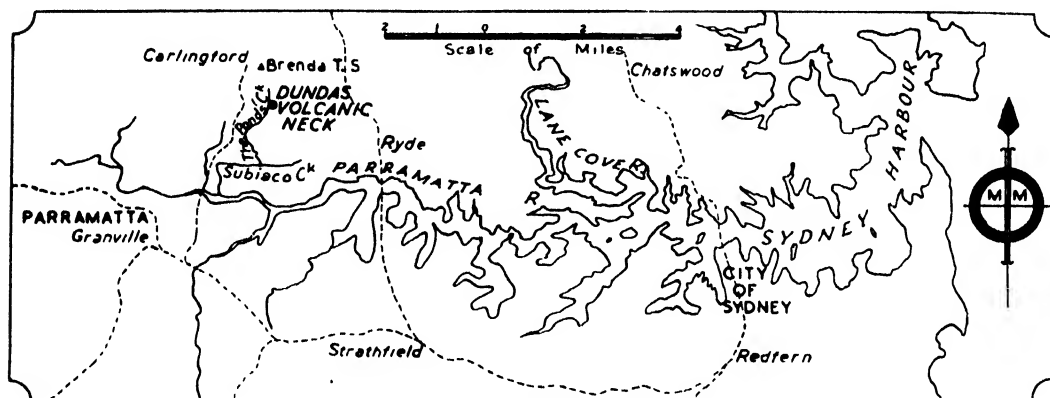


Fig. 1.—Locality Plan.

quarried intermittently during more than 100 years, the excavation now having a maximum length of about 500 feet, width of about 300 feet and being over 130 feet deep. Descriptions of the quarry at various stages of its working have been made by Clarke (1865), Wilkinson (1879) and Benson (1910). Photographs of it taken in 1940 are shown on Plate II.

The work described in this paper was undertaken in 1940-1 to determine whether there were associated with the neck any dykes or other masses of igneous material which were outside the limits of the present quarry. The results were analysed at that time, but were not arranged in a form suitable for publication. Recently it was considered that it may serve a useful purpose to place the results on record, and the present paper has been compiled with this purpose in view. A recent visit has disclosed that since the quarry was surveyed the shape of the floor had been considerably altered by subsequent quarrying operations. The middle bench has now been excavated almost to the same depth as the bottom bench. The floors of both benches were covered by water at the time of the visit and could not be inspected.

The writer wishes to extend his sincere thanks to Mr. J. M. Rayner, B.Sc., F.Inst.P., for his advice throughout all stages of the work and his assistance in obtaining from the Aerial, Geological and Geophysical Survey of Northern Australia the loan of the magnetometer used on the survey; and to his sister, Heather Hanlon, who assisted with most of the instrumental work in the field.

Technical Details.

The base plan, shown in Fig. 2, was surveyed by means of a plane table and telescopic alidade. Approximate heights above sea level are shown by contours, the interval on the undisturbed land surface being 10 feet and in the quarried area 20 feet. The relative heights between points as determined from contours are reasonably accurate, but the relationship of the base station A to sea level has been determined by aneroid readings only.

The magnetometer traverses were laid out on a north-south and east-west grid, the base station for the grid being at B. Magnetometer readings were mostly made every 20 feet along the traverses, although readings as close as 4 feet apart were taken in some critical areas. Readings were made at over 530 different stations, the positions of which are shown on Fig. 3.

Magnetic observations were carried out with a Schmidt type vertical magnetometer, Instrument No. 16128, constructed by E. R. Watts and Son, Ltd. The scale value was 34.9 gammas per division. The instrument was compensated for temperature changes, so that no temperature correction was necessary. Diurnal variation corrections were estimated from repeated check readings at base stations.

No determinations of absolute vertical intensity were made. Base station B was chosen as being representative of the normal vertical intensity throughout the area, in places undisturbed by the presence of basalt or other magnetic material. All values of vertical intensity shown on Fig. 3 are relative to this station.

Throughout this paper the anomalies referred to and plotted as positive would be regarded as negative and vice versa by operators used to working north of the magnetic equator.

Geology and Topography.

The neck consists of a mass of breccia and basalt of Tertiary age, which has intruded shales of the Lower Wianamatta Series (Triassic) and underlying formations. The geology has not been shown on the plan of the area, Fig. 2, because the conventions used would have obscured other details shown. It may be taken, however, that the quarry area practically defines the limits of the main intrusion. The remainder of the area consists of Wianamatta shale, but in most parts the rock is obscured by a cover of soil. Some details of the geology can be seen in the photographs on Plate II. Petrological descriptions of the basalt, breccia and plutonic inclusions found in the neck have been made by Benson (1910).

The neck occupies a hollow, open to the south. The greatest slope is towards the north, rising nearly 300 feet in about $\frac{1}{4}$ mile to Brenda Trigonometrical Station. The Ponds Creek rises to the north and then flows in a channel along the western edge of the quarry. Finally it joins Subiaco Creek, which flows into the Parramatta River (see Fig. 1). The courses of the tributaries of The Ponds Creek show a very close relationship to the areas which the magnetometric survey indicates would be underlain by basalt, as shown on Fig. 2. Portions of the beds of the creeks are overgrown with

blackberry vines, which necessitated breaking the magnetometer traverses at these points. Photographs of some of the terrain over which the magnetometer traverses were made are shown on Plate II.

Magnetic Properties of the Rocks.

No direct determinations were made of the susceptibilities of the various rocks from Dundas. The following notes give probable figures for them.

Basalt.—The susceptibilities of specimens of basalt have been determined by several workers and figures ranging from approximately 500×10^{-6} to $10,000 \times 10^{-6}$ c.g.s. units have been quoted (Heiland, 1940). Samples of Tertiary basalt from Gulgong, N.S.W. (Booth and Rayner, 1933), had a susceptibility of approximately $5,000 \times 10^{-6}$ c.g.s. units. The susceptibility of the basalt from Dundas is probably of the same order.

Breccia.—Benson (1910) describes the breccia as consisting of fragments of shale, sandstone, quartzite, conglomerate, plutonic rocks and basalt. Its susceptibility is probably intermediate between those of the basalt and the sediments.

Shales and Sandstones.—The susceptibilities of these sedimentary rocks would be considerably lower than those of the basalt and breccia. Figures quoted by Heiland (1940) give values up to approximately 50×10^{-6} c.g.s. units for sedimentary rocks.

Results.

The results obtained are shown in Fig. 3. It will be seen that there are three main areas in which magnetic anomalies occur, one to the east of the northern end of the quarry, a second to the north-west and a third to the west of the quarry. In both of the former areas the positive anomaly has associated with it a negative anomaly of either comparable or somewhat smaller value. In the area to the west of the quarry the negative anomaly is either absent or not nearly so marked. The largest anomalies registered were +954 gammas at station 300S/950E and -623 gammas at station 300S/940E, but these were not typical. The largest anomalies on other traverses in the eastern area were ± 300 gammas. In the north-western area the largest anomalies were of the order of +200 gammas, while in the western area the largest anomaly was +175 gammas.

Along the traverse to the south of the quarry there were two points at which anomalies of -125 gammas occurred, but as one of these was adjacent to a wire fence and the other alongside an old dump, it was not considered that these were necessarily associated with masses of igneous rock. It was not possible to obtain a traverse line at this end of the quarry, which would be altogether free from such influences, owing to the presence of buildings, fences, dumps, etc.

The linear arrangement of the magnetic anomalies points to the igneous intrusions in the area being dykes. From their association with the volcanic neck they would obviously be basaltic in composition.

Three magnetic profiles (Figs. 4, 5 and 6) have been included to illustrate certain features of the anomalies. The main points of these profiles will now be described.

Profile O.E., Figure 4.—Along this traverse the readings obtained do not differ markedly from those at the base station O/O, except for the positive anomaly between 240S and 310S. It will be noticed that this anomaly may be due to the composite effect of three separate dykes. On traverses 50E and 50W these three peaks have coalesced to form one relatively narrow peak.

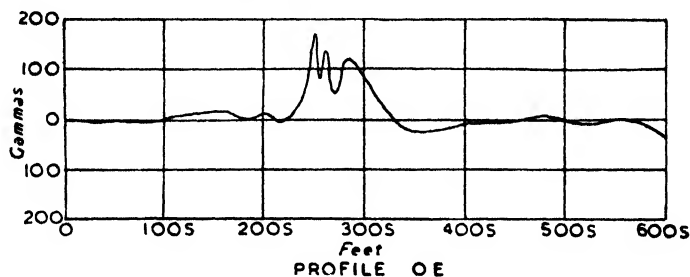


Fig. 4.

Profile 200E, Figure 5.—There are distinct negative anomalies showing on this profile. The first negative anomaly of 105 gammas is associated with a positive one of 160 gammas, while the second negative anomaly of 130 gammas is larger than the associated positive anomaly of 113 gammas. It can be seen from Fig. 3 that, further to the west, the positive anomalies join, one negative anomaly fades out, and the other becomes considerably reduced in magnitude.

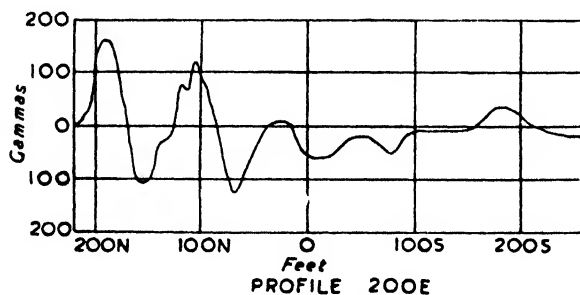


Fig. 5.

Profile O.N., Figure 6.—The only anomaly of any magnitude on this profile lies between 260E and 350E, and consists of a positive and associated negative anomaly. It again has the appearance of being a composite one due to the effect of two dykes, one being in such a position that its positive anomaly is masked by the negative anomaly of the other. The result is peaks of +170 and -12 gammas, with the corresponding negative troughs of -75 and -118 gammas respectively.

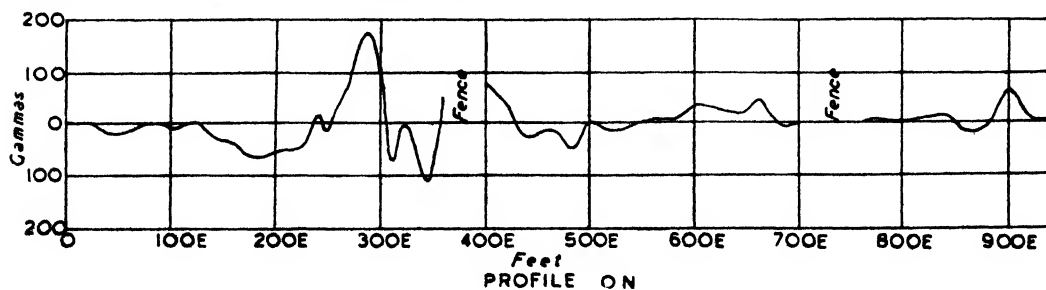


Fig. 6.

In cases where the negative anomaly is approximately equal to the positive anomaly, it is impossible to account for the shape of the magnetic profiles by assuming basalt dykes to be magnetized by induction in the earth's magnetic field only. It seems, therefore, in these cases, that either one face of each dyke possesses permanent south polarity or else the upper surfaces have irregular magnetic polarity. The splitting of the maximum vertical anomalies as shown on Fig. 3 could be due either to the splitting of the dykes which the anomalies represent or else to irregular polarity over the surface of a single dyke. The latter possibility implies a much greater total width of dyke and is considered to be a less likely explanation. Another possible, although perhaps an even less likely explanation, would be that the intrusive masses are more sill-like in character, of limited extent perpendicular to their length, and possess north polarity on one edge and south polarity on the other edge.

The relationship of the dykes to the neck is interesting. It is to be expected that the neck would have been located in an area where the volcanic products could most easily escape, possibly at the intersection of two sets of approximately vertical joints. The extent to which this original joint system might be modified due to strains set up by the intrusion and volcanic activity should be indicated by the disposition of dykes which might fill any fractures so formed. It is noteworthy that the dykes have been confined to three areas, with the possible exception of the area along the course of The Ponds Creek near the south-western corner of the quarry, where it was impossible to find suitable traverse lines. The western magnetic anomaly is approximately on the trend of a dyke which was exposed on the middle bench of the quarry at the time of the survey. Portion of the northern anomaly is also trending towards the neck. The eastern anomaly, on the other hand, does not show any evidence that it is radiating from the neck. The trends of individual dykes are irregular and the evidence is against the formation of any radiating series of fractures caused by the presence of the volcanic neck.

The relationship of the present drainage to the areas in which dykes occur has already been mentioned. This would hardly be so pronounced if the dykes had not originally outcropped. The outcrops have been obscured by weathering, but it is not considered that the weathering would be sufficiently deep or the dip of the dykes sufficiently low to necessitate any allowance being made for horizontal shift between the magnetic anomaly and the sub-outcrop, when calculating the position of the latter.

In order to delineate the probable location of the basalt dykes, as shown in Fig. 2, it has been assumed that there is a dyke, which is approximately vertical, associated with each appreciable positive anomaly. To allow for the possibility that the igneous masses are in the form of either dykes, with irregular surface polarity, or else sills as described above, areas in which an appreciable anomaly of either sign occurs have been classified as possibly underlain by basalt. These areas include those shown as the probable location of basalt dykes.

The only way to determine definitely which of the above assumptions is correct would be to prospect one of the areas by mining operations. In any prospecting outside the boundaries of the present quarry the magnetometric work has enabled the areas likely to be underlain by basalt to be confined to the three shown on Fig. 2. It is considered that the most likely spot for prospecting is the eastern area, because it was here that the anomalies were greatest. Of the two remaining areas the north-western seems the more favourable.

SUMMARY.

The volcanic neck at Dundas consists of a mass of breccia and basalt which has intruded Wianamatta shale. A magnetometric survey has shown that there are three areas adjacent to the neck which seem to have been intruded by igneous rocks. These intrusions are probably basalt dykes, which have weathered outcrops, and tend to split and follow irregular fractures in the country rock.

Plans of the neighbourhood of the quarry showing isogams and probable outcrops of the dykes, as well as examples of the magnetic profiles along some of the traverse lines, have been included.

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EXPLANATION OF PLATE II.

- Fig. 1.—The western face of the quarry, which is situated above and to the right of the inclined tramline, consists of a breccia composed of large masses of practically unaltered country rock, which has been brought up from the underlying sediments. On the extreme right of the photograph the face is composed of basalt. Portion of the floor of the top bench is showing in the foreground.
- Fig. 2.—View of the quarry looking north and showing the top and main portion of the middle bench. The latter has subsequently been further excavated and is now under water.
- Fig. 3.—View of south face of the quarry and portion of the floor of the bottom bench. The floor is now completely under water.
- Fig. 4.—View of the terrain to the west and north-west of the quarry. The base station for the magnetometer traverses is situated near the fence corner in the middle of the photograph. The western edge of the quarry is in the foreground. Just behind the quarry is the channel of The Ponds Creek. The area of the north-western magnetic anomaly is adjacent to this creek near the right-hand side of the photograph. The western anomaly occurs near the small tributary creek on the left of the photograph below the fence.
- Fig. 5.—View looking north-west. The area of the anomaly to the east of the northern end of the quarry is in the hollow in the centre and towards the right of the photograph.
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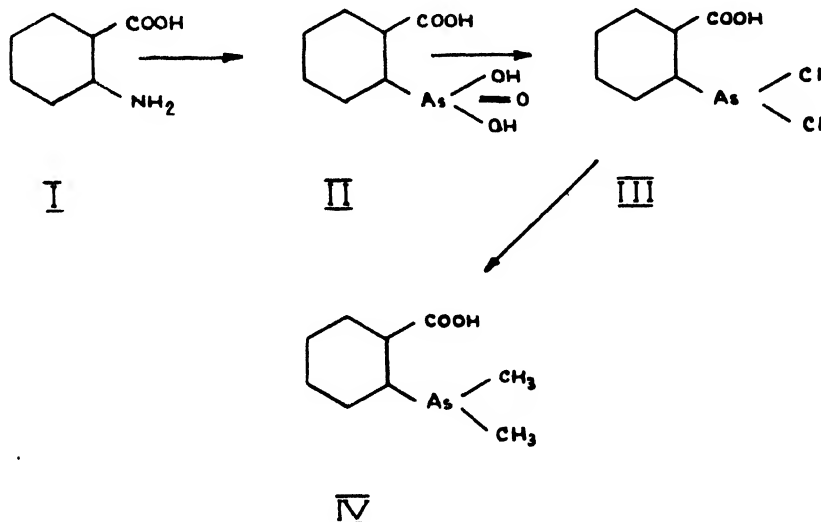
A NOTE ON THE PREPARATION OF SOME
o-CARBOXY-PHENYL-ARSINE DERIVATIVES.

By G. A. BARCLAY, B.Sc.,
and R. S. NYHOLM, M.Sc.

Manuscript received, May 21, 1947. Read, June 4, 1947.

As part of a systematic study of the chelating properties of ortho substituted arsine derivatives, three carboxyl compounds have been prepared. Two of these (III and IV) have not been described previously, whilst the method employed for the other involved certain modifications to that used previously.

Starting from anthranilic acid (I), the following were prepared in succession : o-carboxy-phenylarsonic acid (II), o-carboxy-phenyl-dichlorarsine (III) and o-carboxy-phenyldimethylarsine (IV). The metal complexes of II and IV will be described in subsequent papers.



Anthranilic acid (I) was converted to o-carboxy-phenylarsonic acid (II) using the Bart reaction. Lewis and Cheetham (1923) used copper sulphate as a catalyst in this reaction, but did not describe the pure product. The preparation was carried out with, and without, the use of the catalyst, with no appreciable difference in yields. The pure compound was obtained as shining creamy plates, soluble in hot water.

The o-carboxy-phenylarsonic acid (II) was reduced to o-carboxy-phenyl-dichlorarsine (III) by sulphur dioxide in the presence of hydrochloric acid (Raiziss and Gavron, 1923a). The compound was obtained as white needle-shaped crystals, readily hydrolysed by water. Treatment of o-carboxy-phenyl-dichlorarsine (III) with methyl-magnesium iodide finally gave o-carboxy-phenyldimethylarsine (IV) as colourless, needle-shaped crystals, insoluble in water (Raiziss and Gavron, 1923b).

EXPERIMENTAL.

o-Carboxy-phenylarsonic Acid (II).

Anthranilic acid (92 g.) was finely ground and suspended in concentrated hydrochloric acid (200 ml.). This paste was cooled and diazotized in the usual manner with sodium nitrite (50 g.) in water (100 ml.). Some solid diazonium compound separated out but the whole suspension was added, with constant stirring, to a solution of arsenic trioxide (150 g.) and anhydrous sodium carbonate (310 g.) in water (1,000 ml.). The temperature rose from 30° C. to 40° C., a vigorous effervescence took place and the solution became a light orange colour. After stirring for half an hour, the solution was acidified with concentrated hydrochloric acid, filtered quickly, and allowed to stand overnight. Orange coloured crystals of the *o*-carboxy-phenylarsonic acid crystallized out, being obtained as shining creamy plates on recrystallization from water. Yield, 81 g. (49%). The compound did not melt below 360° C.; it was soluble in hot water, alcohol and sodium acetate solution, but insoluble in benzene and ether.

Found: C=34.02%, H=2.89%. Equivalent weight=123.7.

Calculated for $C_7H_5O_3As$: C=34.17%, H=2.87%; equivalent weight as a dibasic acid, 123.

o-Carboxy-phenyldichlorarsine (III).

o-Carboxy-phenylarsonic acid (50 g.) was dissolved in concentrated hydrochloric acid (500 ml.) and water (200 ml.). Sulphur dioxide was passed through this solution for fifteen hours at ordinary temperatures, the required compound being precipitated. Yield, 50.5 g. (94%). Recrystallization from toluene gave white needles melting at 156° C., which were insoluble in water but soluble in benzene and ether.

Found: C=31.52%, H=1.87%, Cl=26.3%.

Calculated for $C_7H_4O_3AsCl_2$: C=31.48%, H=1.89%, Cl=26.6%.

Note.—The melting point of this compound varies with the time of heating, only melting fairly sharply at 156° C. if placed in the bath at 150° C.

o-Carboxy-phenyldimethylarsine (IV).

o-Carboxy-phenyldichlorarsine (13.4 g.) in dry ether (50 ml.) was added gradually to a solution of methyl magnesium iodide prepared in the usual manner from methyl iodide (22.4 g.), magnesium (5 g.) and dry ether (100 ml.). The ether boiled vigorously and a yellow compound separated out, soon forming an oily, lower layer. The mixture was refluxed for one and a half hours and the complex was decomposed with water. After acidification with hydrochloric acid the required compound was extracted with ether. The *o*-carboxy-phenyldimethylarsine was removed from the ether layer by treatment with sodium carbonate solution and on treatment of the latter with hydrochloric acid the required compound was precipitated. Recrystallization from aqueous alcohol gave 8.1 g. (72%) of the compound melting at 133° C. The compound was insoluble in water but soluble in sodium acetate solution and in alcohol, benzene, ether and chloroform.

Found: C=47.64%, H=4.93%.

Calculated for $C_9H_{11}O_3As$: C=47.80%, H=4.90%.

SUMMARY.

The preparation of *o*-carboxy-phenyldichlorarsine and *o*-carboxy-phenyldimethylarsine from anthranilic acid are described. The use of a copper sulphate catalyst, in the Bart reaction used, was found to be unnecessary.

ACKNOWLEDGEMENT.

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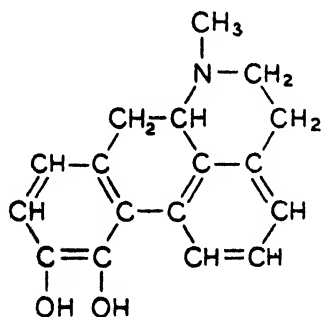
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THE COLORIMETRIC ESTIMATION OF APOMORPHINE.

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Apomorphine, a derivative of morphine, is obtained from the latter by heating under pressure with hydrochloric acid. It is sometimes used as an emetic, 1/10th grain producing vomiting within a few minutes. While processes for the estimation of apomorphine have been described, usually sufficient material is required to give about one grain of alkaloid (Glycart, 1926) and, as less than this quantity may be available, it seemed of interest to investigate the possibility of accurately estimating smaller amounts. Many sensitive reactions have been given for the detection of apomorphine but very few processes have been described for its colorimetric estimation. Walton and O'Brien (1931) described a process based on treatment with bromine. After addition of hydrogen peroxide to remove excess bromine, the solution is heated to bring about a colour change from red to green. The intensity of the final colour is proportional to the concentration of apomorphine. Palet (1918) used Gugliamelli's arsenotungstic and arsenotungstomolybdic reagents for the detection of apomorphine. These give a distinctive blue colour with the alkaloid and the reactions depend on the presence of phenolic hydroxyl groups in the molecule. Consideration of the structure of apomorphine shows that of the two phenolic groups present one has a free para position which is generally believed to be a primary requisite for condensation with a phenol reagent such as 2:6 dibromo-quinone chlorimide—Gibbs' reagent. The method to be described depends on this



APOMORPHINE

reaction in the presence of sodium bicarbonate, followed by extraction of the coloured product into butyl alcohol. The sodium bicarbonate serves to liberate the alkaloid from its salt and at the same time provides a slightly alkaline medium for the reaction. The procedure is simple and rapidly carried out and a distinct difference from the blank is noted with the lowest amount suggested in the range of standards.

EXPERIMENTAL.

(a) Reagents.

- (i) Solution of 2 : 6 dibromoquinone chlorimide, 23 mg. in 5 ml. absolute alcohol—freshly prepared. Gibbs' reagent.
- (ii) Sodium bicarbonate solution, 5% w/v freshly prepared.
- (iii) n-Butyl alcohol—reagent quality.
- (iv) Strong solution of apomorphine. 20 mg. of apomorphine hydrochloride dissolved in 10 ml. of distilled water containing 2-3 drops of hydrochloric acid (1 ml.=2 mg. apomorphine hydrochloride).
- (v) Dilute solution of apomorphine—prepared by diluting one part of strong solution to ten parts with distilled water. (1 ml.=0.2 mg. apomorphine hydrochloride.)

(b) Preparation of Standards.

In a series of stoppered test tubes—not more than half-inch diameter for convenient comparison later—place amounts of the dilute solution of apomorphine ranging from 0.1 ml. to 1.0 ml. with intervals of 0.1 ml. Dilute the smaller amounts to 1.0 ml. with the necessary amount of distilled water. Add *exactly* 0.1 ml. of Gibbs' reagent to each tube followed by 0.5 ml. of sodium bicarbonate solution. Mix well and allow to stand 30 minutes. Extract with 2 ml. of butyl alcohol by shaking vigorously. Allow the layers to separate completely for colour comparison.

A blank experiment on 1 ml. of distilled water should be included. For an estimation take 1 ml. of solution suitably diluted to bring the amount of apomorphine within the above range (0.02 to 0.2 mg.).

The final comparison of colour may be made as soon as the layers have completely separated, after about ten minutes standing.

DISCUSSION OF METHOD.

(a) *Colour of Butyl Alcohol Extract.* Gibbs' reagent gives a clear sky blue colour with phenol and with small amounts the intensity of colour is proportional to the concentration. With apomorphine and the procedure outlined, the colour of the butyl alcohol extract ranges from a slight greenish blue at first, through shades of purple to a bluish purple. Each step is well graduated and a distinctive range of colour is obtained which assists in the estimation of unknown solutions.

The introduction of the purplish shades appears due to further condensation of the blue derivative first formed with excess of the reagent, and for this reason it is necessary that exactly the same amount of reagent be added to each tube. The following experiment illustrates this point.

To several tubes containing 1 ml. of dilute solution of apomorphine were added respectively 1, 2, 3, 4, 5 and 6 drops of reagent, allowed to stand in the presence of sodium bicarbonate and completed as in method. The results are shown in the table.

Amount of Reagent Solution.	Appearance in Aqueous Phase.	Colour of Butyl Alcohol Extract.
1 drop	Clear blue.	Pale blue.
2 drops	Deeper blue with slight turbidity.	Gradually more intense colour of same shade.
3 " }	Range of colour with increasing turbidity.	Off shade first appears—purple tint.
4 " }		
5 " }		
6 " }	Turbidity masks true colour.	Much less blue component obvious.

Thus it will be seen that the off shades were introduced with the larger amounts of reagent.

A second experiment with the same amount of apomorphine and amounts of reagent from 4 to 9 drops confirmed this result. The introduction of the red shade continued with increasing excess of reagent.

(b) *Reagent Solution.* This should be freshly prepared as older solutions give a slight pink extract in the blank. While the lowest tube of the range is still distinguishable from the blank, it is obviously undesirable to introduce additional colour. It should be placed in a brown bottle during use.

(c) *pH of Reaction Medium.* It is interesting to note that the reaction takes place with reasonable speed in the presence of sodium bicarbonate, which gives a pH lower than that recommended for the condensation with phenol. Gibbs (1927) has found that the reaction velocity increases with increase in alkalinity and the rate of condensation with phenol starting with pH of 8.5 has been measured. Apomorphine, however, oxidizes rapidly in alkaline solution and it was considered desirable to reduce the alkalinity as much as possible. The time required for production of maximum colour in the presence of sodium bicarbonate is not unduly long and the result is obtained without interfering colour resulting from the decomposition of the reagent.

(d) *Time Required for the Reaction.* The optimum time was determined by allowing the reaction to proceed for different periods before extraction into butyl alcohol. Using 1 ml. of dilute solution of apomorphine it was found that 20-25 minutes were required for production of maximum colour and shorter periods showed marked difference in the colour extracted.

(e) *Extension of Range of Standards.* It is possible to extend the range to 1.6-1.8 ml. of dilute solution of apomorphine. Where more than 1.0 ml. is used it is advisable to increase the amount of butyl alcohol used for extraction to 5 ml. This reduces the intensity of colour and minimizes the loss of accuracy that otherwise results from the comparison of too deeply coloured solutions.

(f) *Interfering Substances.* It is clear that phenolic compounds which condense with the reagent will interfere with the determination.

APPLICATION TO HYPODERMIC TABLETS.

The tablets were labelled 1/10th grain apomorphine hydrochloride.

One tablet was dissolved in distilled water, 5 ml., containing one drop of hydrochloric acid. One ml. of this solution was diluted to 10 ml. and 1 ml. of the final solution used in the procedure described.

The resulting butyl alcohol extract was equivalent to that from 0.12 mg. of apomorphine hydrochloride (0.6 ml. of dilute solution), which indicates a content of 0.092 grain.

SUMMARY.

A method is described for the colorimetric estimation of apomorphine which depends on the condensation of the alkaloid with 2 : 6 dibromoquinone chlorimide in the presence of sodium bicarbonate and extraction of the coloured derivative into butyl alcohol.

The method has been applied to the assay of hypodermic tablets.

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THEORETICAL ASPECTS OF THE MAXIMUM RECOVERY IN ABSORPTION OR STRIPPING OPERATION.

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(Communicated by Dr. R. C. L. BOSWORTH).

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INTRODUCTION.

The amount of material that can be transferred from one phase to the other in a continuous counter current liquid-vapour extraction system is a maximum when the terminal conditions are in equilibrium. This generally calls for a system containing an infinite number of theoretical plates. This maximum transfer is taken as a basis for the computation of the efficiency of an absorption or stripping system.

Although it is comparatively easy to compute the magnitude of the maximum transfer when but one or two components may transfer from one phase to another, complications arise when the transfer of a multi-component material is under consideration.

Let us consider the general case of the absorption of a multi-component naphtha from the vapour phase by counter-current oil scrubbing with an incompletely stripped oil and equilibrium terminal conditions.

Under the assumed condition of equilibrium at the gas outlet the amount of component C_n absorbed will vary with the volume of oil. For small flows the effluent oil will be charged with component C_n to a state of equilibrium with respect to the entering gas; while, at the other end of the absorber, the emerging gas will not have attained a condition of equilibrium with the entering liquid on account of the limiting volume of the latter. As the oil flow is increased, the effluent oil will continue to be saturated while the condition at the gas outlet will approach equilibrium more closely so that more of component C_n will be recovered. Under the assumed conditions of complete interaction between the two streams there will come a stage at which equilibrium will be attained, with respect to C_n , simultaneously at both ends of the absorber, and under these conditions efficiency of recovery of C_n will attain a maximum.

Further increase in the oil flow beyond this stage will not improve the recovery because the effluent oil will no longer be saturated with respect to the incoming gas. There is consequently a critical oil flow giving equilibrium conditions at both ends of the system; increasing the oil supply beyond that amount would serve no useful purpose so far as recovery of C_n is concerned. However, the critical flow for C_n will, in general, not apply to any other component.

For any critical flow there will generally be only one component which will be present in both incoming and outgoing oils in equilibrium concentrations. Less volatile components will not saturate the rich oil but will be removed from the gas as completely as permitted by their original concentrations in the lean oil. Components more volatile than C_n will be incompletely removed from the gas because the oil will become saturated before the critical oil flow for these components has been reached.

For small transfers, as for example absorption from a lean gas with a high oil rate, the maximum transfer of each component may be calculated fairly accurately by applying the Sounders-Brown (1932) equation for the system containing an infinite number of theoretical plates. For large transfers, as for example absorption from rich gases with low oil rates, this method can lead to appreciable error due to large temperature and volume changes.

Up to the present there appears to have been no general method proposed for the calculation of this maximum transfer and it is the purpose of this paper to attempt to remedy this deficiency.

NOMENCLATURE.

The following nomenclature has been used in the derivation.

Without Subscripts.

L = the total mols of liquid phase entering the system in unit time.

V = the total mols of vapour phase entering the system in unit time.

With Subscripts.

C = the designation for a component.

K' = the equilibrium constant for a component under operating conditions at the top of the column, i.e. liquid entering.

K = the equilibrium constant for a component under operating conditions at the bottom of the system, i.e. liquid leaving.

L = the mols of liquid phase entering the system in unit time for the optimum transfer of a component, i.e. the critical flow for that component.

N = the mols of a component transferred from the vapour phase to the liquid phase in unit time. In stripping operation N is negative.

x = the mol fraction of a component in the liquid entering the system.

y = the mol fraction of a component in the gas entering the system.

Subscripts.

a for the least volatile of the naphtha components.

i for the general component when summing.

m for the most volatile of the naphtha components.

n for the general naphtha component.

$n-1$ for the naphtha component next less volatile than C_n .

p for any naphtha component less volatile than C_n .

$p-1$ for the naphtha component next less volatile than C_p .

q for any naphtha component more volatile than C_n .

$q-1$ for the naphtha component next less volatile than C_q .

DERIVATION.

For the purposes of the derivation the following assumptions have been made:

In unit time a total of V mols of raw gas containing $V \sum_{i=a}^m y_i$ mols of recoverable multi-component naphtha, is contacted with L mols of lean oil containing $L \sum_{i=a}^m x_i$ mols of the naphtha constituents, in an absorption tower operating under the following conditions:

- (1) The oil leaving and the gas entering the system are in equilibrium when there is sufficient of each naphtha component to saturate the oil with respect to the gas.

- (2) The oil entering the system has sufficient contact with the gas leaving the system to establish equilibrium where possible.
- (3) The vapour pressure of the naphtha-free oil entering the system is negligible under operating conditions. If this is not so the oil must be considered as an additional one or more components.

Conditions (1) and (2) normally require that the absorber contains an infinite number of theoretical plates.

Between the top and bottom of the absorption column there exists a pressure difference due to the resistance of the column packing or bubble plates to the gas flow, and a temperature difference due to the liberation of the latent heat of condensation of the absorbed naphtha. In the following calculation it is therefore necessary to use two equilibrium constants for each component, one for the conditions applying at the top of the column, and another for the conditions at the bottom of the column.

If the oil leaving the system has dissolved N_a mols of component C_a and N_n mols of component C_n , etc., by assuming Henry's law, if the effluent oil is in equilibrium with the incoming gas we can write

$$\frac{y_a}{K_a} = \frac{N_a + Lx_a}{L + \sum_{i=a}^m N_i} \dots\dots\dots (1)$$

and

$$\frac{y_n}{K_n} = \frac{N_n + Lx_n}{L + \sum_{i=a}^m N_i} \dots\dots\dots (2)$$

These equations express the condition of equilibrium with respect to components C_a and C_n respectively between the gas entering and the oil leaving the system. On the right-hand side the numerator represents the total number of mols of the component in the oil leaving the system in unit time, while the denominator represents the total number of mols of all kinds in the oil leaving in unit time.

Summing these for the whole of the naphtha gives (for equilibrium with the effluent oil)

$$\sum_{i=a}^m \frac{y_i}{K_i} = \frac{\sum_{i=a}^m N_i + L \sum_{i=a}^m x_i}{L + \sum_{i=a}^m N_i} \dots\dots\dots (3)$$

Equation (3) can be rearranged in the form

$$\sum_{i=a}^m N_i = \frac{L \left(\sum_{i=a}^m x_i - \sum_{i=a}^m \frac{y_i}{K_i} \right)}{\sum_{i=a}^m \frac{y_i}{K_i} - 1} \dots\dots\dots (4)$$

Substituting (4) in (2) gives

$$N_n = \frac{y_n}{K_n} \cdot \frac{L \left(\sum_{i=a}^m x_i - 1 \right)}{\sum_{i=a}^m \frac{y_i}{K_i} - 1} - Lx_n \dots\dots\dots (5)$$

Inspection of equation (5) shows that N_n increases with L . However, there is an upper limit of L for which (1) and therefore (5) will hold because the maximum amount of component C_a that can be transferred from the gas to the

oil in unit time is limited to the difference between the amount entering with the raw gas and the amount leaving in the scrubbed gas which will be in equilibrium with the incoming oil. Therefore, increasing L beyond this critical value L_a will not further decrease the mol fraction of C_a in the gas.

Similarly, a critical value of L , L_n , will be found for the general component C_n beyond which an increase in L will not further decrease the mol fraction of C_n in the effluent gas. Once this stage has been reached for any component it is obvious that the optimum recovery has been obtained. However, a further small quantity will be recovered as the amount of effluent gas is reduced by the further absorption of the lighter components as L is increased. Once L has been increased beyond the critical value, L_n , for the general component C_n there will be insufficient of that component in the system to saturate the effluent oil with respect to the incoming gas.

Consequently equation (1) holds as long as the oil flow does not exceed that just required to give the optimum recovery of the least volatile component, C_a . Since equations (3), (4) and (5) are based on (1) they hold for values of L equal to or less than L_a . However, (2) holds as long as L does not exceed the critical value L_n .

Let us now consider the general case of the naphtha component C_n . As L is increased from $L_{(n-1)}$ to L_n components C_a to $C_{(n-1)}$ will be present in the effluent oil in insufficient quantity to be in equilibrium with the incoming gas, while components C_n to C_m will be present in equilibrium concentrations. Under these conditions (2) will hold but (1) will be invalid.

Summing (2) for components C_n to C_m gives, in parallel with (3) :

$$\sum_{i=n}^m \frac{y_i}{K_i} = \frac{\sum_{i=n}^m N_i + L \cdot \sum_{i=n}^m x_i}{L + \sum_{i=a}^m N_i} \dots\dots\dots (6)$$

whence

$$\sum_{i=n}^m N_i = \sum_{i=a}^m N_i \cdot \sum_{i=n}^m \frac{y_i}{K_i} + L \left(\sum_{i=n}^m \frac{y_i}{K_i} - \sum_{i=n}^m x_i \right) \dots\dots\dots (7)$$

For the naphtha components less volatile than C_n the amount absorbed is obtained from the equilibrium between the incoming oil and the effluent gas (assumption 2) as

$$N_a = V \cdot y_a - K'_a x_a \left(V - \sum_{i=a}^m N_i \right)$$

etc. to

$$N_{(n-1)} = V \cdot y_{(n-1)} - K'_{(n-1)} x_{(n-1)} \left(V - \sum_{i=a}^m N_i \right)$$

Summing these gives (for equilibrium with the incoming oil)

$$\sum_{i=a}^m N_i - \sum_{i=n}^m N_i = V \cdot \sum_{i=a}^{n-1} y_i - \left(V - \sum_{i=a}^m N_i \right) \cdot \sum_{i=a}^{n-1} (K'_i x_i) \dots\dots\dots (8)$$

Substituting the value of $\sum_{i=n}^m N_i$ from (7) in (8) and rearranging gives the nett amount of naphtha transferred from one phase to the other in unit time for oil flow rates between $L_{(n-1)}$ and L_n as

$$\sum_{i=a}^m N_i = \frac{V \cdot \left(\sum_{i=a}^{n-1} y_i - \sum_{i=a}^{n-1} (K'_i x_i) \right) + L \cdot \left(\sum_{i=n}^m \frac{y_i}{K_i} - \sum_{i=n}^m x_i \right)}{1 - \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=n}^m \frac{y_i}{K_i}} \dots\dots\dots (9)$$

In the numerator on the right-hand side of this equation the coefficient of V is the fraction of the naphtha components less volatile than C_n recovered after allowing for losses in the gas leaving the system because of their presence in the incoming lean oil; and the coefficient of L is the fraction of C_n and the more volatile components recovered after making the same allowances. The denominator is a factor correcting the result for the decrease in the amount of gas and the increase in the amount of oil brought about by the transfer of the naphtha from the vapour to the liquid phase.

Substituting this value of $\sum_{i=a}^m N_i$ in (2) and rearranging gives the transfer of C_n in mols per unit time as

$$N_n = \frac{y_n}{K_n} \frac{V \left(\sum_{i=a}^{n-1} y_i - \sum_{i=a}^{n-1} (K'_i x_i) \right) + L \left(\sum_{i=n}^m \frac{y_i}{K_i} - \sum_{i=n}^m x_i \right)}{1 - \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=n}^m \frac{y_i}{K_i}} + L \left(\frac{y_n}{K_n} - x_n \right) \quad (10)$$

Since the minimum concentration of C_n in the effluent gas is $K'_n x_n$ the actual amount thus leaving the system in unit time is given by

$$K'_n x_n \cdot \left(V - \sum_{i=a}^m N_i \right) = V \cdot y_n - N_n \quad (11)$$

If just sufficient oil has been passed to attain this condition (in which case $L=L_n$) the value of $\sum_{i=a}^m N_i$ given by (9) and the value of N_n given by (10) may be substituted in (11) to solve for L_n . This gives

$L_n =$

$$V \left[\frac{\frac{y_n}{K_n} \left(K_n \left(1 - \sum_{i=n}^m \frac{y_i}{K_i} \right) - (K_n - 1) \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=a}^{n-1} y_i \right) - K'_n x_n \left(1 - \sum_{i=a}^{n-1} y_i - \sum_{i=n}^m \frac{y_i}{K_i} \right)}{\frac{y_n}{K_n} \left(1 - \sum_{i=a}^{n-1} (K'_i x_i) - \sum_{i=n}^m x_i \right) - x_n \left(1 - \sum_{i=a}^{n-1} (K'_i x_i) - K'_n \sum_{i=n}^m x_i + (K'_n - 1) \sum_{i=n}^m \frac{y_i}{K_i} \right)} \right] \quad (12)$$

Now that the critical oil flow, L_n , has been determined we may proceed to estimate N_n and $\sum_{i=a}^m N_i$ for all conditions of oil flow.

For values of L less than L_n , N_n is given by (5) and (9) reduces to equation (4).

$$\sum_{i=a}^m N_i = L \cdot \frac{\sum_{i=a}^m \frac{y_i}{K_i} - \sum_{i=a}^m x_i}{1 - \sum_{i=a}^m \frac{y_i}{K_i}} \quad (4)$$

In this case the quantity recovered is independent of the gas flow and directly proportional to the oil flow.

For values of L between $L_{(p-1)}$ and L_p , L_p being equal to or less than L_n , $\sum_{i=a}^m N_i$ is given by (9), using the summation limits of $(p-1)$ and p in place of the

limits $(n-1)$ and n respectively. N_n is obtained by substitution of this appropriate value of $\sum_{i=a}^m N_i$ from (9) in (2) as

$$N_n = \frac{y_n}{K_n} \cdot \frac{V \left(\sum_{i=a}^{p-1} y_i - \sum_{i=a}^{p-1} (K'_{i1} x_i) \right) + L \left(\sum_{i=p}^m \frac{y_i}{K_i} - \sum_{i=p}^m x_i \right)}{1 - \sum_{i=a}^{p-1} (K'_{i1} x_i) - \sum_{i=p}^m \frac{y_i}{K_i}} + L \left(\frac{y_n}{K_n} - x_n \right) \quad (13)$$

In this equation the second function on the right-hand side gives the transfer of the component C_n without allowing for the change in the amounts of the two phases due to the naphtha transfer, and the first function is the correction for this effect.

For values of L between $L_{(q-1)}$ and L_q , where $L_{(q-1)}$ is equal to or greater than L_n , N_n is given by equation (11)

$$N_n = V \cdot y_n - K'_n x_n \cdot \left(V - \sum_{i=a}^m N_i \right) \quad (11)$$

Substitution of the appropriate value of $\sum_{i=a}^m N_i$ from (9) then gives

$$N_n = V(y_n - K'_n x_n) + K'_n x_n \cdot \frac{V \left(\sum_{i=a}^{q-1} y_i - \sum_{i=a}^{q-1} (K'_{i1} x_i) \right) + L \left(\sum_{i=q}^m \frac{y_i}{K_i} - \sum_{i=q}^m x_i \right)}{1 - \sum_{i=a}^{q-1} (K'_{i1} x_i) - \sum_{i=q}^m \frac{y_i}{K_i}} \quad (14)$$

In this equation the first function on the right-hand side gives the transfer of component C_n without allowing for the change in the amounts of the two phases due to the naphtha transfer, and the second function is the correction for this effect.

This equation shows that, as discussed earlier, the recovery of C_n still increases slightly with the oil flow rates above the critical rate L_n . However, for values of L equal to or greater than L_m (14) reduces to

$$N_n = V \cdot y_n - V \cdot K'_n x_n \cdot \frac{1 - \sum_{i=a}^m y_i}{1 - \sum_{i=a}^m (K'_{i1} x_i)} \quad (15)$$

and (9) reduces to

$$\sum_{i=a}^m N_i = V \cdot \frac{\sum_{i=a}^m y_i - \sum_{i=a}^m (K'_{i1} x_i)}{1 - \sum_{i=a}^m (K'_{i1} x_i)} \quad (16)$$

Therefore, for oil flow rates greater than L_m the recovery of the total naphtha or any component is no longer increased by an increased oil flow.

The derivation above has been carried out without consideration of the direction of flow of the different components and may therefore be applied either to absorption (N_n positive and component C_n transferred from gas to liquid), or to stripping (N_n negative and component C_n transferred from liquid to gas). Indeed cases may arise in which both operations occur simultaneously in the one absorber. One particular component may undergo stripping while another undergoes absorption.

In the special case of scrubbing when the absorption oil has been completely stripped before entering the system, i.e. $x_n=0$ and $\sum_{i=a}^m x_i=0$, the critical oil flow from (12) simplifies to

$$L_n = V \cdot K_n \cdot \left(1 - \sum_{i=n}^m \frac{y_i}{K_i} - \frac{1}{K_n} \cdot \sum_{i=a}^{n-1} y_i \right) \dots\dots\dots (17)$$

When the naphtha content of the gas is low, i.e. y is small, (17) approximates to

$$L_n = K_n \cdot V \dots\dots\dots (18)$$

This is the minimum value of L obtained from the Sounders-Brown (1932) equation for complete absorption with a perfectly stripped absorption oil in a column containing an infinite number of theoretical plates.

In the corresponding case for stripping when the incoming gas contains none of the naphtha (e.g. steam) $y_n=0$ and $\sum_{i=a}^m y_i=0$, and (12) simplifies to

$$L_n = \frac{K'_n \cdot V}{\left\{ 1 - \sum_{i=a}^{n-1} (K'_i x_i) - K'_n \sum_{i=1}^m x_i \right\}} \dots\dots\dots (19)$$

and when the naphtha content of the oil is low, i.e. x is small, (19) approximates to

$$L_n = K'_n \cdot V \dots\dots\dots (20)$$

This equation for stripping corresponds with (18) for absorption.

The bracketed functions in (17) and (19) give the quantitative effect in the change in composition of the oil and gas on the critical oil flow for the optimum (and in this case, maximum) transfer of C_n , for the simplified operation.

APPLICATION.

It must be remembered that the relationships and equations that have been derived in this paper are based on the assumption that terminal equilibrium conditions are obtained in the system and that under such conditions they accurately represent the naphtha transfer.

In practice equilibrium terminal conditions are never achieved as the rate of transfer of the naphtha from one phase to the other depends on the difference between the actual and equilibrium conditions. Therefore, for a condition of equilibrium to be achieved an infinitely large surface of contact between the two phases is required and this is equivalent to a negligible capacity for any apparatus of finite size. The approach to equilibrium in different systems varies and can, however, be exceedingly close at times. When only a small fraction of a component is absorbed the absorption is very close to the equilibrium value; the greatest deviation from the equilibrium absorption being with the component whose critical oil flow most closely approximates to the actual oil flow.

These points are perhaps best explained by an example. A slide rule was used for all calculations required.

EXAMPLE.

The following problem is discussed by Horton and Franklin (1940) in the calculation of absorber performance and design.

Absorber operating conditions.

Operating pressure ..	4 Atm.	Absolute.
Oil temperature entering ..	90° F.	
Oil temperature leaving ..	115° F.	

L =lean oil entering 1.00 mols per unit time.

V =rich gas entering 0.9055 mol per unit time.

Analyses. Mol Fractions.

					Rich Gas.	Lean Oil.
Methane	0.286	—
Ethane	0.157	—
Propane	0.240	—
n-Butane	0.169	0.02
n-Pentane	0.148	0.05
Absorption oil (non-volatile)	—	0.93

Since the absorption oil was not completely stripped, equation (12) is used to compute the critical oil flow for each of the components of the gas.

It is necessary to compute only sufficient of these values for two consecutive values to straddle the observed oil flow of $L=1.00$, but they have been calculated for all components for purposes of comparison. The intermediate stages of the calculation have also been included as their preparation greatly facilitates the calculations (Table 1).

Equilibrium constants used in the calculations were read from the nomograph of Scheibel and Jenny (1945, 1947). Since L is straddled by the critical value of the oil flow for propane and butane, the equilibrium transfer of methane, ethane and propane will be given by equation (13) and those of the n-butane and n-pentane by equation (14).

TABLE 1.

					Methane.	Ethane.	Propane.	n-Butane.	n-Pentane.	Oil.
y_n		0.286	0.157	0.240	0.169	0.148	—
y_{n-1}		0.714	0.557	0.317	0.148	0	0
$\sum_{i=a}^n y_i$		0	0	0	0.02	0.05	0.93
X_n		0	0	0	0.02	0.07	1.00
$\sum_{i=n}^m x_i$		53	9.8	3.1	1.15	0.37	0
K_m		0.0054	0.0160	0.0774	0.1470	0.400	—
$\frac{y_n}{K_n}$		0.0054	0.0214	0.0988	0.2458	0.6458	—
$\sum_{i=n}^m \frac{y_i}{K_i}$		46	8.0	2.4	0.77	0.24	Nil
K'_m		0	0	0	0.0154	0.01200	0
$K'_n X_n$		0.0274	0.0274	0.0274	0.0120	0	0
$\sum_{i=a}^{n-1} (K'_i x_i)$		47.2	8.20	2.26	0.6896	0.356	—
L_n		0.0076	0.0226	0.1098	0.1457	0.1281	—
Equilibrium recovery, N_n		0.0087	0.0178	0.1101	0.1407	0.1282	—
Horton and Franklin recovery							

These equilibrium recoveries compare exceedingly well with those computed by Horton and Franklin by plate-to-plate calculations assuming four theoretical plates (Table 1). Actually their figures should be less than the equilibrium figures, but the assumptions necessary for their calculations could readily be responsible for this discrepancy.

From this example it can be seen that the computation of the equilibrium transfer by the method outlined in this paper can be of value in the calculations for absorber or stripper efficiency or design.

SUMMARY.

A general mathematical relationship based on Henry's law has been developed for the maximum transfer of (i) all components, (ii) any one component, of a multi-component mixture from one phase to the other in a counter current liquid-vapour system. Since the maximum transfer calls for equilibrium terminal conditions, the system must contain an infinite number of theoretical plates.

The derivation is based on the absorption of a multi-component "naphtha" from the vapour phase by counter-current scrubbing with an oil that has been incompletely stripped of the "naphtha" components before entering the system. The resultant equations apply to both absorption and stripping operation.

ACKNOWLEDGEMENT.

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THE OXIDATION POTENTIALS OF THE TRIS 1, 10 PHENANTHROLINE AND TRIS 2, 2' DIPYRIDYL FERROUS IONS.

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Tris 2, 2' dipyridyl and tris 1, 10 phenanthroline (o-phenanthroline) ferrous salts are now widely used as redox indicators (Smith and Richter, 1944*b*). By the method of potentiometric titration Walden, Hammet and Chapman (1931, 1933) found the oxidation potentials of the tris 2, 2' dipyridyl and 1, 10 phenanthroline ferrous ions to have the same value, 1.14 volts, in molar sulphuric acid. Hume and Kolthoff (1943) repeated the determination for phenanthroline and obtained a value of 1.06 volts. They assumed that the dipyridyl potential was the same. Smith and Richter (1944*a*) found the dipyridyl potential to be different. In the latter work the potentials were determined as a function of acidity by two procedures: (i) simultaneous potentiometric titration of a mixture of simple ferrous and chelated ferrous ions with a suitable oxidant, and (ii) the ferrous complex was treated with sufficient oxidant to convert one-half to the ferric complex. The results were considered accurate to ± 0.02 volt.

In the present investigation the potentials have not been determined by titration procedures since there is evidence (Dwyer, McKenzie and Nyholm, 1944) that false equilibria may be involved; but instead the oxidized and reduced forms of the complexes have been isolated as the crystalline perchlorates, and then equimolar mixtures prepared in solutions of varying acidity and their potentials determined.

Both systems were found to be unstable owing to the tendency of the oxidized form to undergo reduction, and as a result it has not been possible to apply the Debye-Hückel limiting law for the estimation of the standard potentials.

The potentials were found to fall with increasing ionic strength as expected for a cationic system of this type. However, the stabilities of the two systems were found to be different with increasing acidity. As Smith and Richter (1944*a*) found, the dipyridyl complexes became highly unstable above normal acid concentration. On the other hand the phenanthroline complexes were least stable in weakly acid solution. Since the effect of acid is to form a salt with the basic chelating group, and hence decompose the complex, the behaviour of the dipyridyl complexes is to be expected. The behaviour of phenanthroline is similar to that of the ruthenium compounds (Dwyer, Humpoletz and Nyholm, 1946) and the same explanation, as was put forward in that case, probably also applies, i.e. at the high potentials which occur in the weakly acid solutions the 1, 10 phenanthroline itself is oxidized to 2, 2' dipyridyl 3, 3' dicarboxylic acid.

As a result of these opposite stabilities in acid solution it has not been possible to compare accurately the potentials of the two systems over the whole range of acid concentrations, but in the limited range where a comparison was practicable the phenanthroline potential was usually 28mv. higher.

The dipyridyl ferrous ion is obviously not as satisfactory redox indicator in mineral acid solution as the phenanthroline ferrous ion.

EXPERIMENTAL.

Tris 1, 10 phenanthroline ferrous perchlorate.

Ferrous ammonium sulphate (0.4 g.—1 mol.) was dissolved in cold water (20 mls.), and 1, 10 phenanthroline (0.65 g.—3.1 mols.) stirred in, until completely dissolved. The deep red solution was filtered, heated to 60° C. and perchloric acid (60 per cent.) added drop by drop with vigorous stirring to induce crystallisation. The deep red crystals obtained on cooling were washed with dilute ice-cold perchloric acid and finally with ice water. The substance was dried over concentrated sulphuric acid.

Tris 1, 10 phenanthroline ferric perchlorate.

The tris 1, 10 phenanthroline ferrous sulphate complex was prepared as before, cooled in ice and saturated with chlorine until the colour changed to blue. The mixture was then heated to 40° C. and perchloric acid added as before. The deep blue crystals obtained by cooling in ice were washed with dilute ice cold perchloric acid containing a little chlorine, and finally with ice-cold chlorine water. The filtration was carried out in sintered glass to avoid reduction by filter paper. The substance was finally dried over calcium chloride in an atmosphere of chlorine.

Dipyridyl Compounds.

These were prepared as above, except that the solutions were kept twice as concentrated to compensate for the much greater solubility of the complexes. In appearance the compounds were similar to the phenanthroline compounds; the ferric compound, however, was light blue with a slight green tint.

TABLE 1.

Formulae.	Mol. Wt.	Per Cent.			
		N.		Fe.	
		Calc.	Found.	Calc.	Found.
$(C_{12}H_8N_2)_3Fe(11O_4)_3 \cdot 4H_2O$	867.5	9.69	9.62	—	—
$(C_{12}H_8N_2)_3Fe(ClO_4)_3 \cdot 6H_2O$	1003.0	8.38	8.38	5.57	5.7
$(C_{10}H_8N_2)_3Fe(ClO_4)_3 \cdot 4H_2O$	795.4	10.57	10.68	—	—
$(C_{10}H_8N_2)_3Fe(ClO_4)_3 \cdot 6H_2O$	931.0	9.03	9.03	6.00	6.02

Redox Potentials.

The redox vessel and electrical apparatus were similar to that described in a previous communication (Dwyer, McKenzie and Nyholm, 1944). The potential of the saturated colomel half cell was taken as 0.2442 volts 25° C.

Sufficient of the ferrous and ferric complexes to prepare 50 mls. of 0.0005 M solution of each was weighed in individual small tubes. The ferrous salt was then quantitatively transferred to 40 mls. of sulphuric acid of the appropriate concentration in the redox vessel, traces of residual material being washed in with a further 5 ml. of acid. The material was dissolved as rapidly as possible in a current of purified nitrogen and the ferric salt then added as above. This order of solution tends to stabilize the ferrous/ferric ratio. The potential was determined immediately and at suitable intervals thereafter. With the phenanthroline complexes in solutions of high acidity (5 to 7 N.) the potential rose about 2 mv. in the first ten minutes then fell slowly, until at the end of an hour it had fallen about 5 mv. This was due to decomposition of the ferric

complex as the solution finally changed from purple to red overnight. In the lower acid ranges the potential commenced to fall from the initial value, the rate increasing with decreasing acidity. In the mixture containing no added acid the rate of fall was 2 mv./min. over the first twenty minutes, becoming even greater as time proceeded. The highest potential was accepted as the redox potential. The measurements, which are summarized in Table 2 and Fig. 1, are considered accurate to ± 2 mv., except in the very dilute acid solutions (0.1 N or less), where the accuracy is probably ± 5 mv.

TABLE 2.

Normality of Acid.	Potential in Volts.			
	Authors' Values.		Smith and Richter Values.	
	Phenanthroline.	Dipyridyl.	Phenanthroline.	Dipyridyl.
None added ..	1.120	1.096	—	—
0.01	1.112	1.084	—	—
0.103	1.102	1.071	—	—
0.5	1.086	—	—	—
1	1.073	—	—	—
2	1.057	—	1.06	0.97
4	1.028*	—	1.03	—
5	1.015	—	—	—
6	0.996*	—	1.00	—
7	0.977	—	—	—
8	—	—	0.96	0.92

* From Fig. 1.

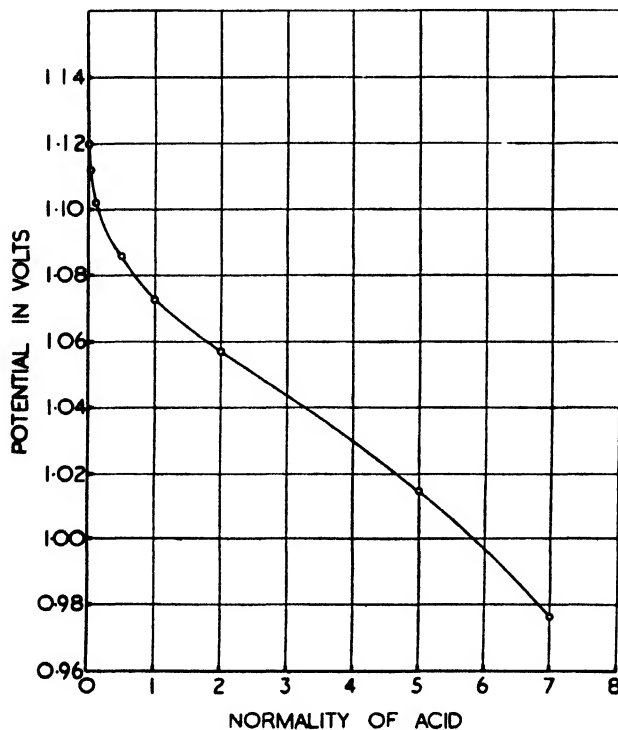


Fig. 1

The potential of the dipyridyl complexes could not be determined satisfactorily above an average concentration of 0.1 N. Even at this acid concentration, the potential fell at the rate of 0.5 mv./min. In the acid concentration of normal and higher it was impossible to obtain a potential value owing to the rapid fall. These solutions became quite colourless overnight, but the red ferrous complex could be regenerated by the addition of alkali.

Attempts were also made to determine the dipyridyl potentials in hydrochloric and nitric acid solutions. While the complexes were somewhat more stable in these acids, the improvement was not sufficient to obtain an accurate measure of the potentials at the higher acidities.

The values obtained for dipyridyl are shown in Table 2.

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SUMMARY.

The redox potentials of the tris 1, 10 phenanthroline and tris 2, 2' dipyridyl ferrous ions have been determined by the standard method of dissolving pure specimens of the oxidized and reduced forms in solutions of varying acid concentration. In 0.103 N sulphuric acid the potentials are 1.102 and 1.071 volts respectively.

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A NOTE ON THE INSTABILITY CONSTANT OF THE TRIS 2, 2' DIPYRIDYL FERROUS ION.

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The instability constant of the tris o-phenanthroline (1, 10 phenanthroline) ferrous ion has been determined by Dwyer and Nyholm (1946) by a redox method, which depended essentially on the observation that ferric iron does not react directly with phenanthroline. The potential of an inert electrode in an acid mixture of ferrous and ferric ions was measured before and after the addition of a known amount of phenanthroline. From the data for the phenanthroline complex and the oxidation potentials of the tris 1, 10 phenanthroline and tris 2, 2' dipyridyl ferrous ions obtained by Smith and Richter (1944), an estimated value of the instability constant of the tris 2, 2' dipyridyl ferrous ion of 1×10^{-15} was obtained. In the present note a direct determination of the instability constant of the tris 2, 2' dipyridyl ferrous ion is described.

In the previous paper it was shown that the instability constant K_I could be derived from the equation

$$K_I = 10^{-\frac{\Delta E}{0.059}} \times C_B^3$$

Where C_B is the concentration of free chelating group and $\Delta E = E_2 - E_1$, E_1 being the potential of the ferrous-ferric couple before the addition of the chelate and E_2 the final equilibrium potential after addition. In the acid solutions employed the chelate is largely present as the ion BH^+ and the concentration of free bases can be obtained from the hydrolysis constant K_H , whence

$$K_I = 10^{-\frac{\Delta E}{0.059}} \times \left[\frac{K_H \times C_{BH^+}}{C_H^+} \right]^3$$

EXPERIMENTAL.

Hydrolysis Constant of 2, 2 Dipyridyl.

Dipyridyl 0.025 g. was dissolved in sulphuric acid (5 mls., 0.1 N) and diluted to 100 mls. with distilled water. The pH, as found with the glass electrode, was 4.74. Making similar assumptions as in the previous paper the hydrolysis constant

$$K_H = 10^{-4.4}, \text{ or } pK_b = 9.6 \text{ at } 25^\circ \text{ C.}$$

Albert and Phillips (1946) by a potentiometric method reported $pK_b = 9.77$ at 20° C.

The instability constant of the tris 2, 2' dipyridyl ferrous ion.

One millilitre each of 0.1 M ferrous ammonium sulphate and ferric ammonium sulphate (0.5 N and 0.25 N with respect to sulphuric acid respectively) were mixed and made up to 100 ml. with dilute sulphuric acid. The concentration of sulphuric acid used was such that the pH of the mixture lay between 1.37 and 2.3 over the four determinations. The pH and redox potential were then determined, and a known weight of 2, 2' dipyridyl added, the weight being in excess of that necessary to form the ferrous complex but insufficient to raise the pH to the point of

precipitation of ferric hydroxide. The mixture was thoroughly stirred and the redox potential and pH determined at suitable intervals until equilibrium was attained. This usually took about an hour. The results are summarized in Table 1. In calculating the mean value and

TABLE 1.

Experiment No.	Initial pH.	Initial Redox. (Volts.)	Wt. of Dipyrldyl (Gms.)	Final pH.	Final Redox (Volts.)	E. (Volts.)	Conc. BH. + (moles/litre).	pK ₁ .
1	2.30	0.450	0.15	2.71	0.667	0.217	0.0066	15.3
2	1.94	0.446	0.1	2.05	0.574	0.148	0.00346	16.9
3	1.37	0.442	0.1	1.56	0.525	0.083	0.00346	17.2
4	1.98	0.446	0.2	2.20	0.666	0.220	0.0098	16.3

standard error of the instability constant the logarithmic transformation has been made, giving a value of $10^{-16.4 \pm 0.4}$. This instability constant is significantly larger than that of the 1, 10 phenanthroline complex ($10^{-17.7 \pm 0.5}$) and is in accord with the observation that the dipyrldyl complex is less stable than the phenanthroline complex. The error in the estimated value for dipyrldyl (10^{-15}) lies in the difference in hydrolysis constant of the chelates and an error in Smith and Richter's value of the oxidation potential of the tris 2, 2' dipyrldyl ferrous ion (Dwyer and McKenzie, 1947).

SUMMARY.

The instability constant of the tris 2, 2' dipyrldyl ferrous ion has been determined by a redox method and found to be $10^{-16.4 \pm 0.4}$.

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POSSIBLE CAUSES OF INTRAFORMATIONAL DISTURBANCES IN THE CARBONIFEROUS VARVE ROCKS OF AUSTRALIA.

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With Plates III-IV.

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I. INTRODUCTION.

Australia possesses some of the most interesting varve rocks in the world. In Carboniferous and Permian times in New South Wales there were at least six glacial stages, and particularly in the peri-glacial lakes of Middle Carboniferous (Kuttung) times there were laid down clays with beautifully distinct seasonal banding. Today these beds are found in a scarcely altered condition, regionally tilted and somewhat folded in places, but for the most part totally unmetamorphosed. In them are bands of remarkable intraformational folds and other disturbances of penecontemporaneous nature, which have long puzzled geologists. No universally accepted explanation has yet been proposed for them.

The best known intraformational contortions in varve rocks are found in the Hunter River Valley of New South Wales, where they were first reported by Sussmilch and David (1919). Others have described them from many parts of New South Wales. They are also known in South Australia. Mawson (1926) noted that the conditions for the formation of varved clays would be found in lakes occupying "over-deepened, rock-bound basins or produced by moraine dams or ice blockages". Such conditions, he observed, were rare during the Permo-Carboniferous in South Australia, but nevertheless, some small examples have been found and in them are contorted layers, e.g. near Normanville, S.A., where there is puckering over a six-inch layer.

Similar contortions are not restricted to varved clays, but often occur in other glacial rocks of Carboniferous and Permian times, such as the glacio-fluvial and glacio-lacustrine sandstones and silts of Victoria, South Australia and Western Australia. More attention, however, has always been paid the disturbances in varved rocks, because of the striking lamination and often perfect preservation of the small structures.

Varve rocks are also believed to be associated with the late pre-Cambrian glaciation in Australia. The Tapley's Hill slates of the Adelaide series of South Australia have often been described as varved deposits, but are now recognized as not actually varved, although strikingly laminated. Their non-varved nature is clear under the microscope. They do not show contemporaneous contortions at their type locality near Adelaide. The regular flexures at Tapley's Hill Quarry and elsewhere appear to me to be tectonic, though the rocks admittedly must have been folded while still very plastic. From another locality, however, apparently also of late pre-Cambrian rocks (Mawson's Torrowangee series) at Campbell's Creek, near Poolamacca, north of Broken Hill, N.S.W., Andrews and Browne collected an example of contemporaneously contorted varved shale, which David (1922) exhibited alongside Seaham samples to the 1st Pan-Pacific Science Congress, at Honolulu in 1920. Intraformational disturbances are also known in many other horizons of the Adelaide series (Howchin, 1920), a fact which I have recently been able to confirm at many points in the Mt. Lofty and Flinders Ranges.

The object of this paper has been to discuss Australia's best-known contorted glacial beds, in the varves of the Hunter River area, and, bearing in mind evidence of other examples, to attempt an explanation of general validity for this type of intraformational contortion.

II. THE NATURE OF THE DISTURBANCES.

1. Discovery of the Carboniferous Varves in the Hunter Valley.

The discovery by David of tillite in the Kuttung series of the Hunter River Valley on the British Association excursion in company with Penck and Coleman on 22nd August, 1914, led to the discovery of widespread glacial remains of Carboniferous age in this area. Permian glacials of course had been known here since the days of Oldham. In 1919 Sussmilch reported the presence of varved rocks here; he had no hesitation in interpreting them, as in North America and Europe, as the result of alternating seasonal deposition of glacial material in a lake. No one doubts this interpretation in view of their typical "varve" structure, their association with striated boulders in the adjacent tillites, and remembering the striated pavements of unquestionably glacial origin at Wolfingham, only nine miles N.W. of Maitland, New South Wales (Osborne and Browne, 1921). In the other States similar relationships are known in the Permian, as at Hallett's Cove and Inman Valley, South Australia, and at Bacchus Marsh, Victoria.

Referring to Sussmilch and David (1919) on the Hunter River Valley exposures, we read: "At intervals in the varve shales there occur layers which

are strongly contorted, similar to those described by Sayles from the Squantum Beds. These contorted layers range from a few inches up to four feet in thickness, and display in miniature every type of Alpine folding . . ." (see their plates XXIV, XXVI and XXVII). "A bed which is contorted in one part may fade out into a part which shows no contortion at all, while the contorted layers themselves are interstratified between perfectly regular unfolded layers. The whole evidence suggests that the contortion is contemporaneous . . ."

2. Opinions on the Structures at Seaham.

So far, so good, but what of the cause of these contemporaneous contortions? Sussmilch suggests that they are "due to the stranding of floating masses of ice, or perhaps in some cases to the temporary forward movement of the ice front" (*loc. cit.*, pp. 272, 273). David (1922) suggests "the movement of ice in some form tending to develop horizontal gliding planes". It is very interesting to note (in Sussmilch, *loc. cit.*) that "delicate, but well-preserved annelid tracks are found in the bedding planes of some of the varve shales", proving that the beds are water-laid, and thus cannot be dismissed as "englacial melts" (see Carruthers, below). A similar case of contorted structures in varves containing arthropod tracks is known in the European Pleistocene (Schwarzbach, 1938).

In the following years Osborne carried out an extensive survey of that part of the Hunter Valley area where these glacial lake beds are best exposed, especially around the abandoned town site of Seaham (1922*a* and *b*; 1925*a* and *b*; 1927). Without making a special study of varve contortions, he followed in general the opinions of David and of Sussmilch. Osborne made a notable contribution, however, in pointing out that "peculiar relationships between some of the varve rocks and either sandy or tuffaceous rocks are to be found in many parts of the area" (1925*a*, p. 75). With great kindness he has personally shown me sections illustrating this "intimate co-mingling of the two units, shale and tuff or sandy sediment. At times there is a suggestion that the tuffaceous material has been injected into the varve rock, while at other times the reverse seems to be indicated." Rightly, I think he rejected any idea of intrusion, recognizing the disturbance as contemporaneous, and gave two alternative suggestions:

- (a) "The structures may possibly be explained by considering the effect of differential movement (gliding) upon a series of partially consolidated sediments" (1922*a*, p. 183).
- (b) "Other structures . . . seem . . . to have been produced as a result of the dragging force of moving ice . . . Layers of twisted varve rock pass into breccia bands, followed by more shale, and finally massive tuff."

Evidently the two had been laid down normally in succession, some of the tuff hardening more quickly than the varve clay, which one would expect would keep its plasticity for some time. At this stage, he concluded, a movement of ice interfered, producing shattering, injection and foliation. Contemporaneous erosion and current scour were also noted in the varves.

In 1935, for the Melbourne A.N.Z.A.A.S. meeting, Sussmilch restated his opinions on the cause of the varve contortions as follows: "Such folding is contemporaneous, and must have taken place while the varve layers were still soft, and must have been caused by ice movement of some kind, possibly the dragging movement of stranded masses of floating ice along the lake bottom. It has been suggested that it might have been caused by the "slumping" of layers of inclined sediment, but the whole of the evidence indicates that the varves now contorted were deposited as practically horizontal layers, consequently gravity could not have come into operation." There is a big difference,

however, between apparently or "practically horizontal", as we shall see in Part III, Section 7, where it is suggested that in fact slumping may occur on slopes so gentle that they could not normally be detected by the eye.

The Swedish geologist Caldenius, from de Geer's Institute for Glacial Chronology in Stockholm, visited Seaham later and made a special study of the varves (1938). Recognizing the contemporaneity of the contortions with the sedimentation, he gives two explanations, the disturbances being due, he says,

(a) to "small slidings during the time of the existence of the lake", or

(b) to "the readvance of the land-ice".

The ribboned structure with thickening and thinning suggested slides to him (p. 362). Most of the contortions, he says, originated from settling of some part or other of the lake bottom. They might also be formed when "pebbles and blocks from drift ice had fallen down to the bottom or when icebergs, weighed down by their moraine burden, had sunk" (p. 361). In this case, we may note, an intercalation of tillite should be found adjacent to the disturbed beds, and such is the case in one place (see p. 358). Caldenius also remarks that even where the varves appear to be of a more distal nature (in relationship to the source of material at the snout of the glacier), contortions still occur.

The roadsides and quarry at Seaham rapidly became a geological "classic" after their initial discovery, so that David took steps to have the quarry in particular preserved as a cultural monument. Osborne recounted to me how, at the Pan-Pacific Science Congress excursion here in 1923, the assembled scientists clambered all over the quarry, rediscovering in miniature all the tectonic structures they knew so well from the Alps. This analogy with Alpine tectonics serves to illustrate my own interpretation, as we shall see in due course.

3. Other Examples.

Elsewhere in the Hunter River valley area it is the same. For example, Carey (1937) describes how, at the gap west of Werrie Creek, "the varves are 250 feet in thickness, and towards the top there is a sudden disposition to contortions, yielding some beautiful specimens, due to the impress of over-riding glaciers of an advancing ice-sheet" (p. 365). They are overlain by tillite which may be taken as representing a glacial readvance; so his interpretation is apparently supported by this. On the other hand, at another place, his "Landslide Section", we read how in a three hundred-foot section of varves the contortions occur in the lower parts (p. 347). In this case they are not immediately overlain by tillite, as one would expect if they had been due to a glacial readvance.

The same appears to be true in the Gosforth district, where Browne found good examples of contorted varves at certain well-marked horizons (1926, p. 242); his best section was one-quarter of a mile west of Mr. B. Cant's house. Another good locality is Browne's Creek near Currabubula (15 miles west of Tamworth), where Benson (1920) found a section of varves overlain by mudstones. He sketches a typical example of contorted varves in his fig. 4 (p. 298); in his fig. 5 he shows a rounded granite boulder, which not only bends down the underlying varves, but minutely crumples them *on one side only* in the manner of exotic blocks in the Alpine "Wildflysch", where gravity sliding is generally called in to account for the distribution of large boulders rather than the agency of floating ice. Angular granite blocks are shown in Benson's fig. 6. It is not suggested, of course, that floating ice is out of the question here; quite the contrary, but it is perhaps well to consider other possibilities.

Looking farther afield, in rocks more of Permian than of Carboniferous age, to Victoria, South Australia and Western Australia, we note that varve shales are

rarer (see Mawson's example, noted above), though intraformational contortions are common enough in the glacio-lacustrine sandy formations, e.g. in glacio-lacustrine sandstones in the lower quarry at Bald Hill, two miles N.W. of Bacchus Marsh, Victoria (Summers, 1923, notes how the "peculiar crumpling in the sandstones has been ascribed to the action of stranding ice"); again, in the River Finniss glacial sandstones of South Australia (Howchin, 1910, illustrates them and explains them as "produced by the ploughing movement of ice-masses"); in Western Australia, in the glacial sandstones of the Lyons series of the North West Basin (Raggatt, 1936, speaks of "the pushing action of grounding ice rafts"). Some of the Finke River, S.A., contortions appear to be similar (David and Howchin, 1923).

4. Types of Structures Involved.

My own impression of the intraformational contortions in the varves at Seaham and elsewhere is that there are four principal types of structure:

- (a) Large overfolds, sometimes grading into overthrusts or "nappes", involving up to ten or more individual annual varve layers, and ranging in amplitude up to 3-4 feet high (see Fig. 1, and Plate III). They rest on normal flat-lying beds and are in turn overlain by flat-lying beds. The contact with the latter is an erosion plane. The direction of the overfolding is generally the same in any one outcrop, but I was not able

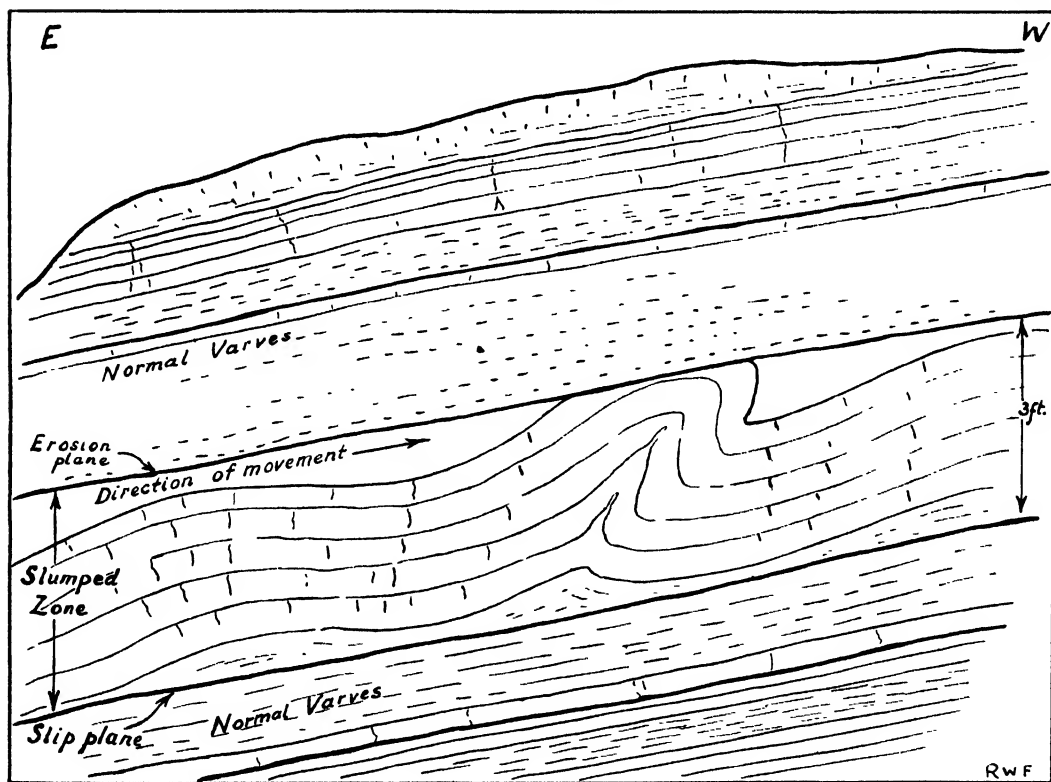


Fig. 1.—Characteristic slumped zone in Carboniferous varves at Seaham Quarry, N.S.W. Such perfect form is only obtained by movement in coherent, yet highly mobile strata. Note that the quarry face here is at about 45° to the direction of slump. The dip is about 30° S.S.W., while the slip occurred on a slope directed from N.E. to S.W., i.e. roughly in the same direction, but before the introduction of the present steep slope by subsequent tectonic action. (From a photograph by the author: see also Plate III.)

to make a regional study, in order to work out a directional analysis of any significance. This, however, might be a fruitful project for the future.

- (b) Ribbon-like overfolds, grading into overthrusts and imbrications, or "schuppen" and miniature "nappes" (using Alpine terminology). Generally only one annual layer is involved, often a fairly thick and competent one. The layer involved would belong to the year preceding that of the movement. This layer appears to have come "unstuck" and become folded over and piled up together, while the soft mud of the contemporary year fills in the loops and cracks. Folds and "schuppen" will range in this way up to about six inches in height. The beds above and below these are normal (see Fig. 2, and Plate IV).

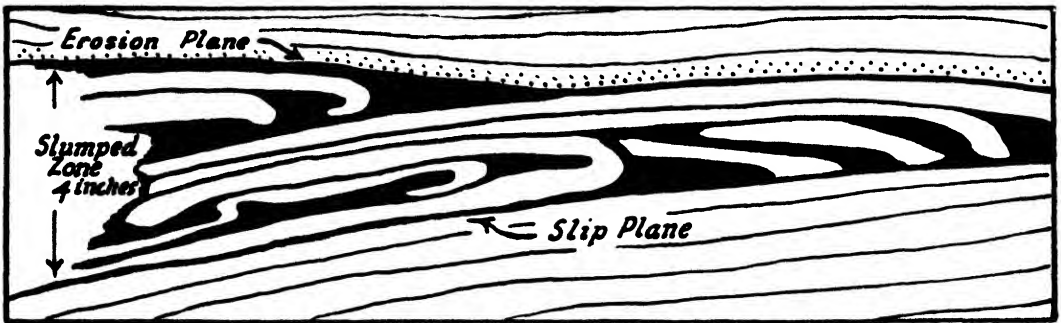


Fig. 2.—Ribbon-like overfolds and miniature "nappes" at Seaham. Note how the varve layers of particular years have become "unstuck" and moved more or less independently of one another. (From a photograph by the author; see also Plate IV.)

- (c) Fine layers of foreset beds with micro-contortions, usually not more than one inch high, between the normal beds above and below. These are therefore restricted to the contemporary year. Current scour, contemporaneous erosion and redeposition can be observed (see Fig. 3).
- (d) Zones of brecciation or injection, such as described first by Osborne (1925a), occur intercalated between normal strata in the same way as the first three structural types.

Experience overseas, in North America and Europe, together with a thorough examination of the literature, has suggested to the author that the type of structures encountered elsewhere in glacial varves is generally much the same. In addition to the four principal types listed above there are many associated or secondary types. The sliding block mentioned by Benson, for example, may be included here.

5. Distribution of the Structures.

From the distribution of these contemporaneous disturbances certain conclusions can be drawn:

- (a) The disturbances in a definite area appear to affect certain zones more than others. Higher and lower in the section, irregularities will be rare, until one comes to the next contorted zone. Browne, in particular, noted this interesting characteristic (1926).
- (b) A comparison of the regional sections by Sussmilch and David, Osborne, Carey and others, show that the disturbances in the varves do not occur at the same zone over any great distance, and will then switch suddenly to another zone, or die out altogether.

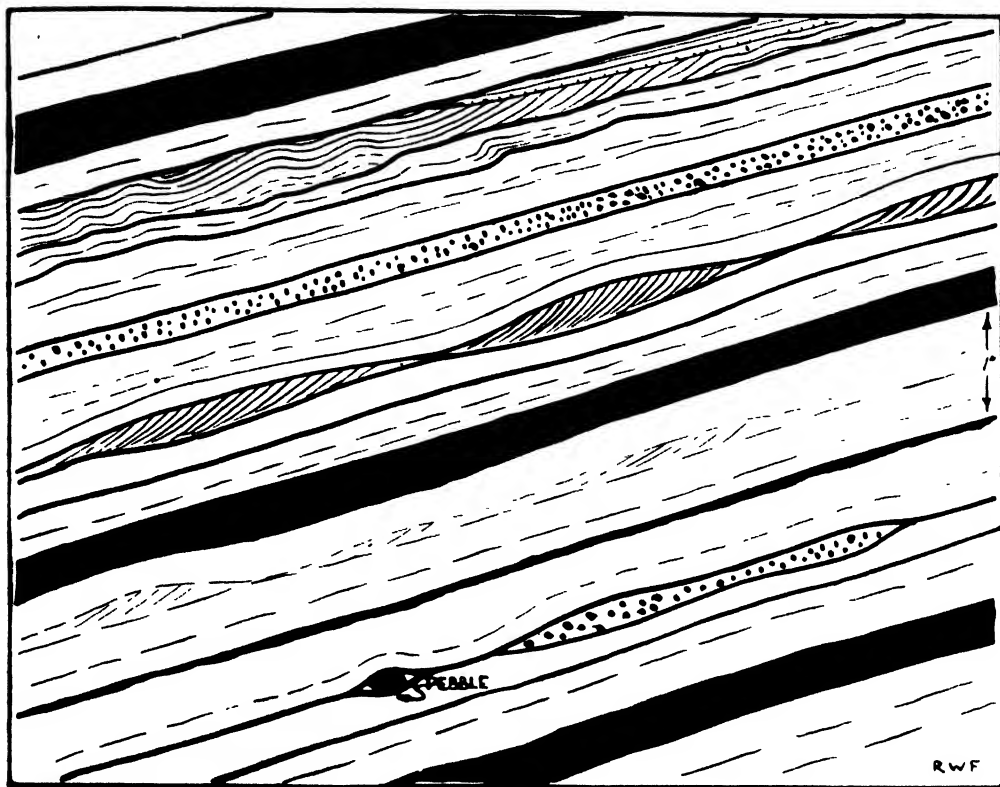


Fig. 3.—Fine layers of foreset beds with micro-contortions restricted to contemporary years, indicating local currents of temporary duration. (From a photograph by the author.)

- (c) The zones of disturbance in the varves do not reappear in any definite cycle. In some places they are overlain by tillites, but in others by great thicknesses of undisturbed varves, or by tuffs, mudstones or sandstones. This feature is most important, for, if the crumpling were due to glacial readvance, the contorted varves should always be overlain by a till, deposited by the retreating ice. It may be argued that the advancing ice pushed from one side, but this is quite impossible in these examples as neither over nor underlying beds are affected; alternatively, if the till that should theoretically be overlying the contorted horizon has actually been eroded away, no sign of this intense erosion is apparent, and no erosion relics are left.

III. REVIEW OF THE POSSIBLE CAUSES OF GLACIAL CONTORTION IN GENERAL.

In the expression "glacial contortion", we embrace all atectonic (i.e. non-diatrophic), pseudo-tectonic and even some *apparently tectonic* disturbances in sediments associated in any way with glaciation. We shall deal with seven possible causes for this glacial contortion here. Amongst these a fairly wide field will be covered, even when it is quite clear in advance that certain ones cannot possibly apply to our Australian examples.

Examples of many of these types of glacial contortion are believed to exist in nature, though the relative importance of each may be hotly contested.

Certain other suggestions have been made from time to time regarding the origin of special cases of contortions in glacial beds, but the application of these

seems to be generally so infrequent or improbable that we cannot consider them here more than very briefly. For example, Emerson (1898) described certain little folds in the Pleistocene varves of Northampton, Massachusetts, as due to contemporaneous, subaqueous currents; considering his figure 39, we are certainly reminded of Lamont's current-induced "anti-dune structures" (1939). Emerson certainly seemed to be right here, but in another case, his figure 38, there is a most obvious case of slumping as we now interpret it, yet he said "The quiet water allowed the clay layers to form and then the strong current crumpled them" (*op. cit.*, p. 647).

And then again there was the suggested explanation by Shaler (in Shaler, Woodworth and Marbut, 1896, p. 969) for a four-inch bed of contorted clays which could be followed for over fifty feet in the Upper Merrimac valley (New Hampshire). Rightly rejecting glacial thrust, on account of the limited vertical range of the disturbance, he made the (then) rather novel suggestion that the sediments might have increased their bulk by some chemical reaction, such as the kaolinization of the clays. This chemical expansion process, called by Grabau (1924) "enterolithic", is now well known, but I doubt if it could be used to explain contortions in shale alone.

Lahee (1941) has included solifluction in his list of possible contemporaneous contortions, and unquestionably certain types of disturbance in glacial beds may be attributed thereto, though these would not normally be found in water-laid sediments, and in any case solifluction structures are often so characteristic that they are not usually mistaken for anything else. Nevertheless, certain structures known as "sticks" found below the German Pleistocene are ascribed to pre-Glacial leaching by Keilhack (1931), but are almost certainly due to solifluction.

A sort of differential creep has been envisaged by some authors. Sayles (1919, p. 38), speaking again of the New England Pleistocene varves and their contorted horizons, suggested a "creep toward an unsupported edge due to the weight of superincumbent clays alone". Miller (1922), who was a great exponent of differential drag as an explanation for many types of micro-tectonic structures, came to much the same conclusion about the same occurrences. Under the load of the overlying sediments, that is, by gravity, in a delta-fan for example, the more argillaceous beds are supposed to have crumpled and moved sideways while the sandier beds remained in place. In another place, Sayles (1919, p. 23) considered that differential shearing was produced at a lower horizon while a glacier ploughed through the beds several feet above. These concepts are hardly supported by the evidence; for one thing—in most of the New England varves there is but little lithological difference as a rule between the disturbed and the undisturbed layers. Further, the upper contact of the contorted zone is always a contemporaneous erosion plane with a local unconformity, and the overlying layer often shows an upwards grading from coarse to fine in the grains of sediment.

It is probably undesirable to spend more time on these rather exceptional cases, and so we shall now proceed to deal with the seven most usual explanations, more or less in the order in which they have become generally known.

They are as follows :

1. The grounding of ice-floes and icebergs.
2. The push of glacial readvance.
3. Post-glacial tectonics and differential movements.
4. Melting of frozen mud and "dead ice".
5. Disturbance due to subglacial dragging.
6. Structures preserved by englacial melting.
7. Gravitational slumping.

1. The Grounding of Ice-floes and Icebergs.

This was the first and still is the most popular explanation ; it was suggested by James Geikie (1874), and possibly even earlier authors. The idea is that drifting or wind-driven ice-floes or icebergs scrape along the sea or lake floor, rumpling the fresh sediments and displacing some of them. Stockton (1890) observed such grounding of ice-floes on the shores of Arctic seas. Priestley, on the Scott Antarctic Expedition, noted how the fauna on the sea floor near the shores was completely obliterated by the effect of grounding ice. Kindle (1924) reproduced a photo showing folds three feet high on the Arctic shores of Alaska. Koch and Teichert have noted the powerful effect of Arctic winds on sea ice in Greenland and I myself have been impressed by them in Canada. The objection, however, to this phenomenon being applied as an explanation for the contortions in the varved shales of Seaham type is that there is no evidence of an external crushing force, but rather of an evenly-applied force, which must be internal, since the strata above and below the disturbance are not touched.

Perhaps the best known locality for intraformationally folded zones in seasonally banded clays is in the Connecticut Valley region of New England, U.S.A. (see, for example, works by Emerson, Shaler, Sayles and others). For the last fifty years, certainly, the most favoured hypothesis here for explaining these contortions has been that of "glacial grounding". Unquestionably, certain of these structures, which range from an inch or so up to 20 feet in thickness, are due to a variety of other causes, as will appear in due course, but the bulk of them show constantly repeated features, that absolutely preclude the possibility of physical contact with floating ice. For example, the contorted zone is often thin, of constant thickness, underlain by normal sediments (the plane of separation being one of mechanical disturbance), but smoothly cut off above by erosion and unconformably overlain by another series of normal sediments exactly parallel to those below. There is abundant evidence of contemporaneous disturbance in the sedimentation, current phenomena, cross-bedding and ripple-mark, but often none of mechanical impact. As a rule there is no deposit of boulder clay such as would be deposited by the melting ice which is supposed to have grounded on the lake floor.

In exceptional cases, however, there is a layer of boulder clay above the contorted varve horizon (see, for example, Sayles, 1919, fig. 1). At the Woods-ville clay pit, New Hampshire, several zones have this overlying layer of till. Sayles says (*op. cit.*, p. 19): "It would appear as if an iceberg of considerable size had dragged over the bottom, destroying some layers, contorting many of those below, and leaving a deposit of till on the top and there pressing pebbles down into the folded bands."

In the bulk of cases where there is no till, Sayles admitted that "it is difficult or impossible to decide what caused the movement" (*op. cit.*, p. 38) though, in explaining some of the plates, he suggested that one could imagine for these cases that icebergs had tipped upside down and crumpled the varves with their clean, formerly upper surfaces: an ingenious explanation indeed. In any case, it is extraordinarily hard to visualize how the passage of an iceberg could scrape up and crumple a single zone, say four inches thick, over exactly the same horizon for hundreds of feet, and yet not disturb the underlying beds at all. In terms of alpine tectonics, this would entail the explanation of a superficial "décollement" (disharmonic folding) by means of a "traîneau *écraseur*": a patent impossibility. The occasional presence of pebbles and boulder clay above the contorted zone can quite satisfactorily be explained by any melting of floating ice, without requiring an actual mechanical collision (see, for example, Sverdrup, 1931).

Another series of typical intraformational contortions in laminated shales, similar to those at Seaham, but at Squantum, Massachusetts, has been described

by Lahee (1914) to be the result of grounding floe-ice, an idea accepted also by Sayles (1919). First, he said, the ice crumpled the zone and secondly more floes came along and neatly carved off the tops of the resultant folds. Sayles (1914) noted a current-bedded sandstone overlying them in one place and suggested that running water might have truncated the beds. As to the contortions themselves, in many cases no trace remains of the impact of grounding ice in the form of a compressed and macerated surface, or of boulders or lenses of tillite (such as would result from the melting of the ice-floe) in the immediate vicinity of the disturbances.

The age of these Squantum beds has been provisionally put as Permian or Carboniferous, but even this must not be regarded as more than a rough estimate, and it is possibly in part due to "wishful thinking", a desire to make it contemporaneous with the Permian and Carboniferous glaciations of the southern hemisphere (see Dunbar, 1924, and others). In fact, serious doubts have been cast by several authors (Köppen and Wegener, 1924, p. 33; van der Gracht, 1928, p. 221; Salomon-Calvi, 1933, p. 103) on the actual evidence for glaciation in the Squantum beds, pointing out that neither seasonal banding (contrary to Lahee's opinion, 1914), nor "tillite-like" boulder beds are absolute criteria for it. I would like to draw attention to a similar association of absolutely *non-glacial* sediments forming today at the Dead Sea in Palestine. Banded seasonal shales (Lisan marl series) are associated in places with enormous boulder beds, which are produced under seasonal arid conditions; and in associated mud-flows the boulders often receive pseudo-glacial striations.

Thus, in spite of claims made by J. Geikie, Chamberlin, Atwood, Lahee, Sayles, Twenhofel, Sussmilch, David and others, I do not believe any fossil example of this "glacial grounding" has been definitely proven. Slater, one of the greatest glaciologists in Britain today, has remarked (1926) that one of the chief errors of the so-called Agassiz school of glaciologists has been "the over-emphasis of floating ice as a geological agent". In spite of this warning, the error still persists, though the alternative possibility of gravitational slumping has received some rather tentative consideration in recent years, as shown, for example, by an illustration of typical intraformational folds in the Massachusetts Pleistocene varves "caused presumably by slump or the pushing of grounded bergs" (Jahns and Willard, 1942, pl. 2).

2. The Push of Glacial Readvance.

This is the next most popular hypothesis, postulating that, as a glacier readvanced, pushing into its own peri-glacial lakes and streams, both its end-moraine and its peripheral glacio-fluviatile and glacio-lacustrine beds would crumple. Twenhofel (1932, p. 748) suggests that there will be a zonation, grading away from the end of the glacial advance: "brecciation will be nearest the ice, succeeded outward by a zone of thrust-faulting and over-turned folds, and beyond this by a zone of low or gentle folding". Certainly end-moraines show this sort of disturbance (see Lamplugh, Reid, Slater, Lewis, Keilhack and Salomon), but I do not believe that any such zonation over large areas of water-laid sediments has ever been seen in nature. In a glacial readvance the preexisting beds would tend to become frozen solid, and neatly sheared off (Slater). Bailey pointed out that the snow and ice overlying frozen sediments would act as a gliding plane. The type of folding normally found in varves is open and free and the sediments seem to have been soft, saturated and mobile. An external pressure applied to any unconsolidated sediment cannot be transmitted far by that sediment. Maceration results, not folding.

3. Post-glacial Tectonics and Differential Movements.

As remarked above, we are dealing only with structures in beds of glacial origin, water-laid or melted out from decaying glaciers that appear to be atectonic (i.e. non-diastrorphic). Yet some of these structures have been interpreted as resulting from post-glacial tectonics. In general this hypothesis is discounted, but in the North American Pleistocene certain of these structures, which we regard as definitely contemporaneous, have been described by Miller (1922) and others as due to differential tectonics, in one form or another.

First objection is the fact that the Pleistocene is remarkably free from tectonic disturbance and that a differential horizontal movement would require considerable orogenic forces or contrasted elevation (to permit gravitational down-sliding, also postulated by Miller). Secondly, the commonest types of intraformational disturbance in glacial sediments exhibit an erosion plane above the folding; differential movement would require a gradual transition or a definite slip plane here. Of all the possible causes of glacial contortion this type is regarded as the least probable. An example in western Canada, regarded by Allen as tectonic, has already been identified as due to glacial action (type 5, below) (Slater, 1926). Exceptional cases may be encountered in regions where the fractures of block-faulted zones continued moving while the sediments were still forming. Such is definitely the case in parts of eastern Europe (von Bubnoff, 1936, p. 1482) and in parts of North America (Mathew, 1894, etc.). In such cases the type of disturbance should be self-evident as a rule, and would not normally be confused with other types.

4. Melting of Frozen Mud and "Dead Ice".

The accepted explanation for certain intraformational contorted glacial beds has long been the melting of a sheet of intercalated frozen mud, producing internal collapse with some lateral readjustment (see mention in A. Geikie, 1903, etc.). Stagnant patches of "dead ice" eventually melt out, giving the same results. It is clear, however, that this method requires certain conditions which are not present in many of the contorted beds. For example, evidence of roof-caving and collapse should be obvious. Lateral slumping would only be associated with it as a secondary feature. Such an explanation could scarcely be considered for the examples in the Seaham varves, since the latter are firstly not of tillite material, and secondly, are overlain conformably by other varved shales.

5. Disturbance Due to Subglacial Dragging.

This would be a scraping movement in the style of the Alpine "traîneau écraseur". A glacial readvance is postulated, but a different mechanical process is involved. Instead of glacial push, we have a sub-glacial drag. We should expect to find a capping of boulder clay or till, which will melt out when the glacier retreats. The disturbance will be more like deep-seated tectonics with high angle thrusts and imbrications. Such phenomena are definitely found in nature. Here we have some of the glacial pseudo-tectonics which are so well known in the Pleistocene of Europe (e.g. von Bubnoff, 1936, p. 1481) and North America (e.g. Emerson, 1898; Antevs, 1928). To this class will be restricted those disturbances which affect the basement, or floor of the glacier. Examples of this were shown by Slater in Norfolk (1926), Suffolk (1927*a*), Germany (1927*b*), Denmark (1927*c* and *d*), Alberta (1927*e*) and elsewhere; and in Australia, at Bacchus Marsh, by Jacobson and Scott (1937). If boulder clay is involved, and especially if angular blocks of the country rock are found embedded in contorted boulder clay, then it is highly probable that there has not only been subglacial drag, but also englacial melting (see below). In fact, the two are practically inseparable.

6. Structures Preserved by Englacial Melting.

This is a fairly modern theory based on the observation of contortions in the actual ice of glaciers themselves, which have developed during the laminar movement of the ice sheet (Hamborg, 1908 ; Phillip, 1920). In the advance of glaciers, material scraped off the floor is carried forward and upwards ; the flow movement of the glacier produces contorted folds and overthrusts within itself very similar in appearance to those of Alpine tectonics. It is argued that, when the glacier melts, this material is deposited *in situ* and preserves the same contorted structures. The material will consist of boulder clay (till), plus exotic blocks carved off from the irregularities of the glacial floor and carried up along the thrust planes within the glacier. In boulder-clays and tillites, therefore, we may expect to find these pseudo-tectonics or "fossil glaciers" (Chamberlin, Phillip, Gripp, Slater, Richter, etc.). Since glacial flow is conditioned by gravity, the type of tectonics will emulate that found in the superficial Alpine folding, though some deeper-seated tectonics are also to be expected, as a result of subglacial drag. Frequently imbrications of the country rock, Cretaceous, Eocene, Oligocene and Miocene, are involved with the Pleistocene glacial materials (Geikie, Kayser, Keilhack, Wahnschaffe, Slater, Shaler, Woodworth, Veatch). Exotic blocks encountered under these conditions in north Germany occur up to half a mile in length. Slater describes them in England as "giant erratics". In both north Germany and North America, complex folding, shearing and thrusting are found parallel to the old morainal fronts in the Pleistocene englacial material.

Water-laid sediments will not be encountered in this englacial material unless it is in the form of these "exotic blocks". There is no doubt that our undisturbed varved clays, with clear evidence of seasonal deposition and contemporary life, were water-laid and therefore could not have been involved in these glacial pseudo-tectonics. An example of this englacial melting, however, with exotic masses of water-laid varved rock introduced into the till, is noted, and correctly interpreted by Carey (1937, p. 358) from the Werrie Basin, N.S.W. Another example was recorded at Bacchus Marsh (Permian) by Jacobson and Scott (1937). It appears likely too that the contorted patch of glacial sands intercalated in the tillites on the Finke River, S.A., described and illustrated by David and Howchin (1923), belong to this group. These authors ascribed the disturbances to a glacial push, but Ward (1925) regarded the associated contorted tillites as englacial melts. Sayles (1914) described how fragments of the varved slates at Squantum are now found in the overlying "till". This he interpreted as subglacial dragging, but a laminar movement of the ice-sheet followed by englacial melting could just as well have brought it into its present relation with the "till". Easier still, ordinary sedimentary conditions could have produced this relationship.

Mention should be made at this point of the Carruthers hypothesis (1939). Carruthers believed that the "banded clays" and varved rocks of Britain were not water-laid, but were boulder clays, given a false stratification by the laminar movement of glaciers, which had subsequently melted. Melting is supposed to start at the base and work upwards. In this way, he argued, perfect pseudo-morphs of the internal structure of glaciers would be preserved in those banded clays and silts, which are normally attributed to glacio-lacustrine deposition. This hypothesis was most thoroughly examined, discussed and eventually rejected by the bulk of speakers at a meeting of the Geological Society in London. The discussions, however, served to show that the bulk of the glacio-lacustrine contortions were regarded by Bailey, then Director of the Geological Survey of Great Britain, and other competent speakers, as typical gravitational slumping phenomena. And this leads us logically to our last type of contortion in glacial beds.

7. Gravitational Slumping.

Gravitational slumping takes place in water-laid glacial deposits under penecontemporaneous subaqueous conditions. As noted above, when Carruthers displayed photos of certain contorted glacial beds to the Geological Society in 1939, Bailey, Trotter and others immediately pronounced them to be gravitational slides, "exactly comparable to the slump effects so well known in the geosynclinal Lower Palaeozoic rocks of Scotland and Wales" (see fig. 6b).

Hitherto the subject has received but little attention, although recognized in specialized conditions, such as the melting of the ice enclosing subglacial streams, when lateral slumping will occur in the resultant eskers (Flint, 1928). This fact is well recognized by de Geer (1940) in the "ose" (or esker) ridges of Sweden. Twenhofel (1932, p. 740) quite clearly says: "Glacial deposits not uncommonly are held up by ice against or over which they have been deposited. As the ice melts away, slumping takes place with possible deformation of the strata." However, most previous observers have attributed such contortions to one or other of the six possible sources of disturbance listed above.

Hadding, after making a thorough study of gravitational slumping in Sweden (1931, p. 390), noted evidence of it in the late Pleistocene there; he mentions how Munthe had attributed this particular folding to glacial readvance, but argues that this "may not be possible, after we have seen how structural forms of the kind present here are typical of subaqueously slid strata".

In his wonderful new study of the Swedish varves, de Geer (1940) definitely recognizes the rôle of slumping in causing local disturbances in his geochronological varve scales, for he says (p. 28), "Sliding of many or single varves has occurred especially where the slope was steep and when a locality became elevated above water-level and its counter-pressure thereby was annihilated. Sometimes the whole bunch of slidden varves has got their thickness falsified, sometimes the sliding has affected the lower varves only, while the upper ones have preserved their normal thickness." This phenomenon, however, was only recognized within narrow limits and many illustrations in his work are labelled as due to iceberg grounding, when the evidence is all for slumping. He recognized, however, that normally the grounding iceberg would leave a layer of till.

After naming half a dozen possible types of contemporaneous disturbance (including grounding ice-floes and icebergs, subglacial drag and solifluction), Lahee in his well-known textbook on "Field Geology" (1941, p. 192) also recognizes that saturated muds will slide at only 2-3°. "The resulting structure, though closely resembling the contemporaneous deformation due to grounding ice blocks, is likely to be of wider extent in the plane of stratification. Isolated boulders and other evidences for the former presence of ice might serve as a means of discrimination were it not for the fact that there is nothing to prevent mud flows in bodies of water in which icebergs are floating." As we have seen at Seaham in particular, there is a *notable absence* of erratic boulders or glacial débris in the vicinity of the contorted beds.

As far as I am aware no reference to the possibility of slumping in the lakes of the Glacial period in the north of England can be found before the 1939 discussions. In America, however, half a century ago, McGee (1891, p. 469) appears to have been the first to recognize it, when he attributed the contortions in the Pleistocene beds in Muscatine County, Iowa, to "inequipotential slipping . . . of the most readily yielding beds" (see Fig. 4). Other contorted beds there, however, showed the usual symptoms of our type 5 (subglacial drag) and these he recognized for what they were. Subsequent authors were not so observant, either ignoring the structures or attempting to generalize on one or other of our first six above-mentioned types. Miller (1922) performed a service by rejecting, point for point, No. 1 of these types (glacial grounding), but unfortunately only in an endeavour to prove a certain theory of his own

(differential movement), which is not supported by all of the observed facts in glacial beds.

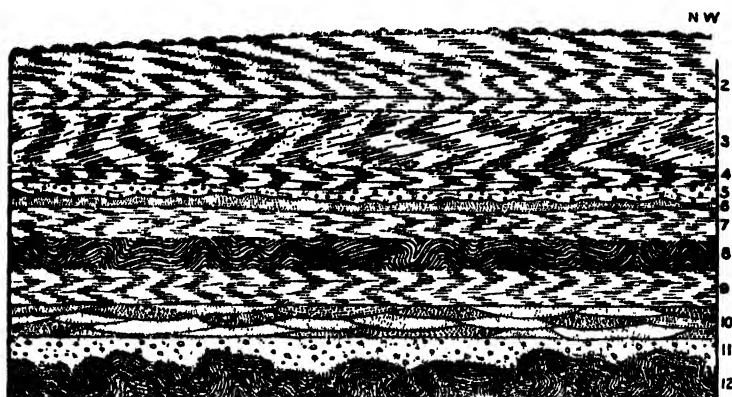


Fig. 4.—The contorted glacial beds which were first recognized as due to slumping. This section from Muscatine, Iowa, was drawn by McGee (1891, fig. 59). The contorted beds are well laminated silty clays of fluvio-glacial origin; the lower horizon is overlain by a gravel and the upper by a similar silty clay.

Slumping was apparently considered by Sayles (1914), for the Squantum contorted slates, but he did not have the advantage of having Arkhanguelsky's results of 1930 and did not appear to have considered the works of Heim (1908) or Hahn (1913). He remarked: "In view of the fact that the layers above and below the folds have not been deformed, it is difficult to see how the folds could have been formed by simple gravity, especially when it is noted that the folding and deposition were contemporaneous." As will be seen in the following, it is precisely these criteria which are characteristic of gravitational slumping.

Let us, then, review this slumping question.

(a) *General Conditions Required for Slumping.* It is found that submarine slumping is very common today, especially on steep lake floors, continental slopes, etc., and often under the stimulus of slight seismic vibrations. With suitable sediments (water-saturated intercalated muds and sands) Arnold Heim (1908) had observed that slipping on a large scale takes place on a lake slope of two to three degrees. As a result of extensive soundings and samplings with a coring tool in the Black Sea, Arkhanguelsky (1930) has even demonstrated

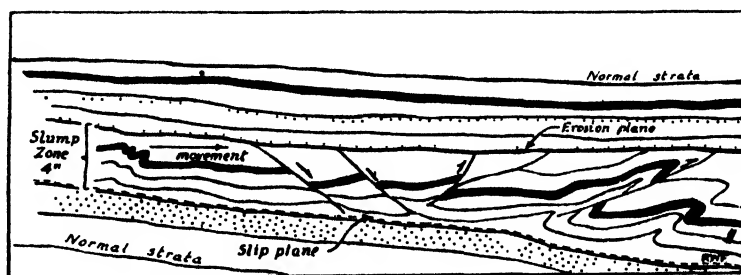


Fig. 5.—Contortions due to gravitational slumping, obtained artificially at the lower end of a 5-foot tank, tilted to only 7°. (In nature, on the grand scale, a similar effect is often obtained on an even more gentle slope.) After the irregular surface of the slumped beds had been eroded flat by the introduction of a slight current, it was then covered over by further sedimentation. Note juxtaposition of simple folds, overthrusts and tension faults.

slumping at under one degree in rather carbonaceous muds, but he found that sliding takes place *everywhere* in the soft superficial beds when the slope is over two or three degrees. Milne (1897) in studying submarine cable-breaks, demonstrated that slumping was often the cause and that it might take place on any slope of over one and a half degrees average declination. In the latest work on sedimentation, Kuenen (in Trask, 1939, p. 353) says, "as soon as this slope became more than a few degrees the deposits start to slide down".

The water actually supports the sediment in some cases, and slumping only sets in when that support is removed. Kindle (1917) observed contortions in the soft mud-flats of the Bay of Fundy in Canada, near the mouth of the Avon River. When I was there I noticed that when the tide went out the support was taken away from the newly deposited muds, and slumping set in. It was a striking coincidence when, without previous prompting, a keen local naturalist, Mr. Enright of Maitland, N.S.W., described to Dr. Osborne and myself just such a case of slumping in the bank of the Hunter River there many years ago after a high flood level had subsided. The slide has been subsequently hidden under a retaining wall to prevent similar slides.

Experiments have been carried out to show that slumping will actually take place in a laboratory tank, e.g. by J. Thoulet (1891, 1904) and more recently by R. E. Rettger (1935). Their results show structures that we know well in nature. Those interested should compare the photos of our supposed slumping in glacial beds with those of experimental slumps and some of the classical examples in nature, e.g. in the Ordovician at Trenton Falls, New York State (Hahn, 1913), near Girvan, Scotland (Henderson, 1935), and near Dublin, Ireland (Lamont, 1938); in the Silurian of Wales (Jones, 1939); in the Devonian of Gaspé, Canada (Logan, 1863); in the Jurassic of Sweden (Hadding, 1931); in the Solenhofen limestone of Germany (Walther, 1904); in the Tertiary of the Caucasus (Kugler, 1939); in the Miocene of Öhningen, Germany (Heim, 1908); and, most recently, in the Miocene near Florence, Italy (Beets, 1946). (See Figs. 6a, b, c, 7a, b, c.)

Here in Australia we have many examples of such contortions. In the Hawkesbury Sandstone in the Sydney region, these were attributed to slumping in the A.N.Z.A.A.S. "Handbook for New South Wales" (1932). This observation (by Dr. W. R. Browne, I believe) is the first actual reference to the Hawkesbury contortions as "slumping". Previous authors (e.g. Sussmilch, 1922, p. 161) say "no really satisfactory explanation of this feature has yet been suggested". Although nothing has been printed on the subject as yet, I understand that some years ago S. W. Carey prepared a short, unpublished paper on these structures in the vicinity of Long Bay, Sydney, as part of his university studies. Howchin (1920) found numerous examples of intraformational disturbances in South Australia (mainly in the Proterozoic) and recognized "subaquatic gliding deformation, which takes place on a gently sloping sea or lake bottom, by which the sediments become broken up, contorted and brecciated" (p. 307).

(b) *Summary of Criteria for Slumping.*—What do all of these structures have in common that distinguishes them from other small disturbances?

- (i) Contorted beds are intercalated between parallel undisturbed beds.
- (ii) The disturbances are on a small scale ranging from an inch or two to not more than 50 feet in amplitude.
- (iii) They do not usually show a *direct* connection with local tectonics, as, for example, does drag folding (see Nevin, 1936, for distinguishing features).
- (iv) Complicated folding takes place without well-developed associated cleavage.

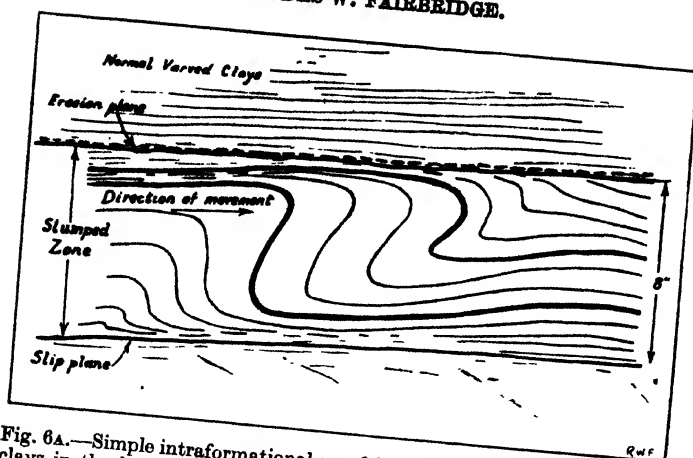


Fig. 6A.—Simple intraformational overfold in typical Pleistocene varved clays in the bank of the Connecticut River, two miles east of Northampton, Massachusetts. (From a photograph by Miller, 1922, fig. 5.)

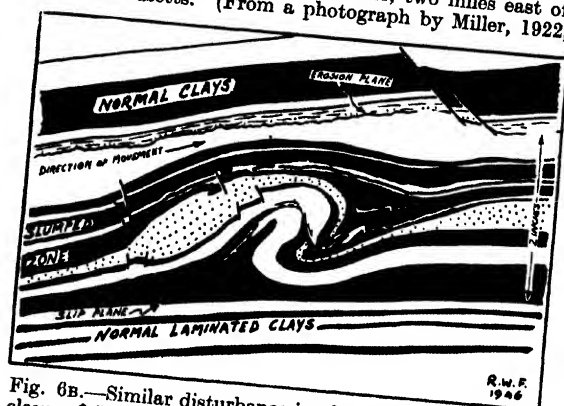


Fig. 6B.—Similar disturbance in the Pleistocene glacial clays of England (Coatham Stob, Durham). From a photograph by Carruthers (1939, Plate XXI, No. 4), of structures described by Trotter and by Bailey as "typical slumping". (See Carruthers, 1939, p. 330.)

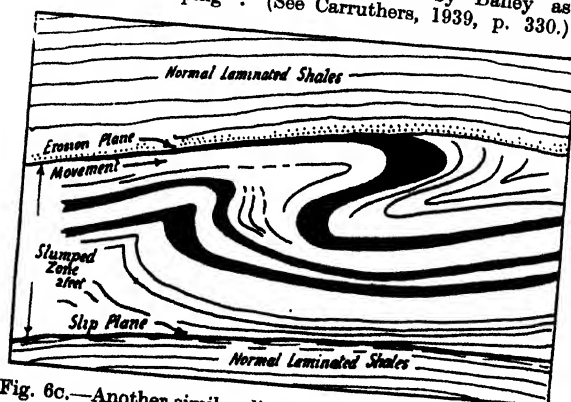


Fig. 6C.—Another similar disturbance, but this time in the non-glacial Lisan marls (Pleistocene) of the Jordan Valley, north of Jericho, Palestine. (From a photograph by the author.) The above drawings should be compared with out Fig. 1 and Plate III, showing similar structures in the Carboniferous varves at Seaham, N.S.W. Comparisons of this sort may be made with non-glacial slump folds from all parts of the world.

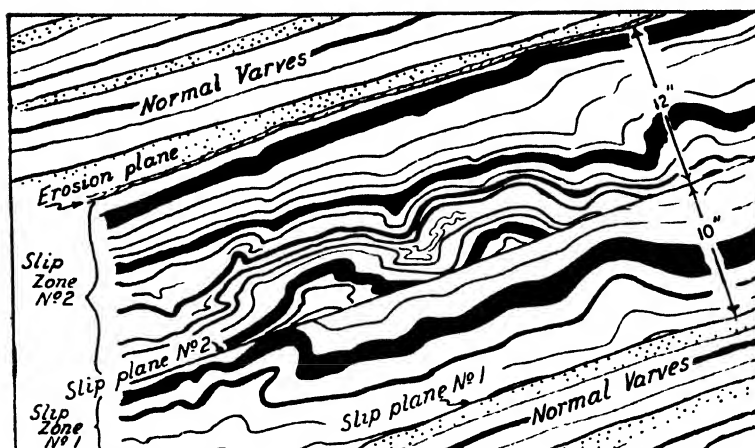


Fig. 7A.—Double slumped zone in Carboniferous varves at Cant's Quarry, Hillsborough, N.S.W. Slip zones numbers 1 and 2 are probably penecontemporaneous, but No. 2 has come from higher up the original slope, overriding No. 1. The section is almost certainly not at right angles to the original slope. Complex structural forms are due to the originally highly saturated nature of the beds. (From a photograph by Dr. W. R. Browne.)

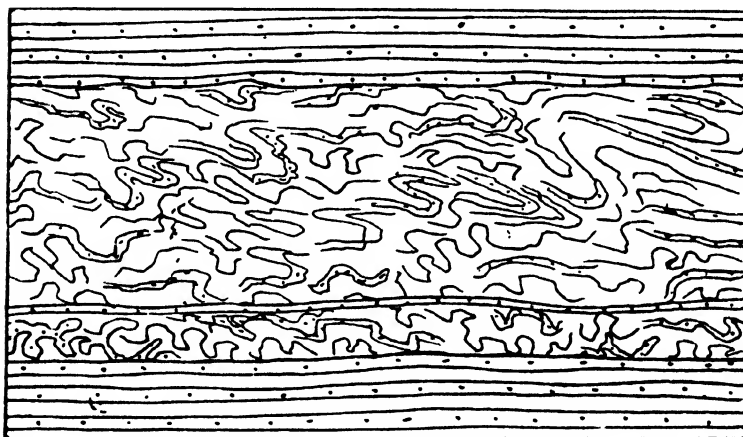


Fig. 7B.—Zones of contorted and dismembered beds in Pleistocene varved clays and silts at South Street clay pit, Northampton, Massachusetts. (From Miller, 1922, fig. 6.)



Fig. 7C.—Non-glacial example of fragmental "ribbon" contortions in Devonian limestones of Gaspé, Canada (after Logan, 1863, fig. 425). Now regarded as due to submarine slumping (Crabau, 1924; Twenhofel, 1932; and others). The slump zone varies from 7 to 10 feet in thickness.

- (v) Softer beds tend to flow into the gaps, brittle beds sometimes snap.
- (vi) There is no recrystallization or mineral orientation.
- (vii) The lower contact is normally a slip-plane.
- (viii) The upper contact is normally a local erosion plane.

While perhaps not all these criteria are always identifiable, at least the majority should be readily seen, even in fairly small outcrop. A regional survey of course should provide corroborative evidence.

(c) *Causes of Slumping in Glacial Beds.* Certain causes of gravitational slumping, as found in glacial beds, are restricted specifically to glacial conditions, while other causes of it may be encountered in any sedimentary deposits. It is generally simple enough to identify gravity slumping as such, but the precise identification of its cause cannot be seen from an inspection of the site alone, but requires a widespread regional study. We shall deal with possible causes in their probable order of importance in glacial beds.

- (i) A glacial lake is often dammed up by an ice wall; when the wall partly melts from time to time, the water support for the unconsolidated sediments will be removed and they will slump, only to be covered by more sediments when the ice returns and enables the water level to rise once more. The ice dam is often supplied by a glacier, which explains the apparent paradox that the water will actually return with a further cold period.
- (ii) In an ice dam formed by a moving glacier, open crevasses will come opposite the end of the lake from time to time and a certain quantity of water will suddenly escape into the opening, in the manner of steam into a slide valve. The release of water will cause a partial removal of support as in type (i) and smaller scale slumping will take place.
- (iii) Slumps will cause a sudden displacement of water at the bottom of the lake, setting up sudden currents, in the manner described by Sieberg (1927) for the origin of tsunamis in large-scale slumping (see also Gutenberg, 1939). Contemporaneous subaqueous erosion will be caused by these currents and the sediment removed will be redeposited and often slumped on an almost microscopic scale.
- (iv) A glacial stream debouches into a glacial lake building up a delta. Overloading will gradually occur and slumping will set in to restore the slope to its angle of rest.
- (v) Deposits in subglacial streams (later to form kames and eskers) will be supported as long as the ice lasts. As melting sets in the retaining walls will disappear and the unconsolidated sediments will slump outwards. Practically all kame and esker deposits are affected in this way (Flint, 1928).
- (vi) A glacial readvance may buckle and pile up the deposits at the head of the lake. These folds will not be transmitted to the further sediments as the material is as yet only partially consolidated. The pressure will cause the deposits nearest the glacier to rise up, thus providing a long outward slope, descending into the lake. Slumping will take place down this inclined plane.

(d) *Distribution of Slumping in Glacial Beds.* There appear to be large numbers of examples of slumping in glacial beds in the Pleistocene of Great Britain, Scandinavia and Germany, in Canada and the United States (illustrations, variously interpreted, may be found in Carruthers, 1939, see our Fig. 6b; J. Geikie, 1874; Wilson, 1918, see our Plate III; Miller, 1922, see our Figs. 6a and 7b; McGee, 1891, see our Fig. 4); in the Permo-Carboniferous in South

Africa and the Congo (Haughton, 1930 ; Fourmarier, 1916 ; Boutakoff, 1934) ; in the Carboniferous of New South Wales (Sussmilch and David, 1919) ; late pre-Cambrian of the Tien-Shan Mts. (Norin, 1937), and also South Australia (Howchin, 1920). Of these by no means all are restricted to varve shales ; some of the intraformational disturbances are in fluvio-glacial sands, some in glacial silts or stratified clays.

In the Kimberley Division of Western Australia, I myself noticed several horizons of these structures in the Permian sandstone cores from the Nerrima deep test-well of the Freney Oil Company in 1941. Raggatt (1936) has illustrated a contorted sandstone from the Lyons series (Permian) of the North-West Basin ; it underlies one of the glacial boulder beds (the boulders are believed to be dropped from floating ice), and Raggatt's conclusion was that the contortion " is clearly due to the pushing action of grounding ice rafts which deposited the boulders ". He goes on to mention another example (there are many) in the bed of the Arthur River, where it is overlain by the Callytharra limestone. The sandstone is almost vertical, but the limestone dips at only 2-3°. Normal (conformable) relationships are seen a few yards upstream. In this case there is no evidence of débris from grounding ice rafts, and yet the contortion is the same. The first example, I would have considered as inconclusive, but the second may well be due to a slump phenomenon.

8. Criteria for Distinguishing Different Types of Disturbance in Glacial Rocks.

For general purposes, a few simple rules may be suggested for distinguishing the various disturbances encountered in glacial deposits :

- (a) If contorted beds are *englacial* (not water-laid), e.g. boulder clay or till (" Primary " of Slater, 1929, p. 457), the disturbance will be due to :
 - (i) The push of glacial readvance (contortion adjacent to, or overlain by till).
 - (ii) Subglacial drag (contortion overlain by till).
 - (iii) Englacial shearing and subsequent melting (contortion in the body of, or at base of a till).
- (b) If contorted beds are *subaqueous* sediments, e.g. glacio-fluviatile, glacio-lacustrine, eskers, etc. (" Secondary " of Slater, *loc. cit.*), the disturbances will be due to :
 - (i) Grounding of ice-floes, etc. (contortion adjacent to, or overlain by till).
 - (ii) The push of glacial readvance (contortion adjacent to or overlain by till).
 - (iii) Subaqueous slumping (contortion overlain by penecontemporaneous, water-laid material of some sort).

IV. CONCLUSIONS.

When we compare the features of the principal intraformational folded beds of Seaham, New South Wales and elsewhere in Australia, described in earlier papers and referred to in Section II of this paper, with the seven different possible types of glacially contorted beds, we are forced to reject each, on one count or another, until we come to the last. And our conclusion may be stated quite simply thus :

The bulk of intraformational folded beds in the Carboniferous of Australia exhibit recognized characteristics of gravitational slumping and relatively few suggest direct glacial impact. The slumping is very likely due to the periodic release of water from impounded glacial lakes, overloading, and other well-recognized causes.

V. ACKNOWLEDGMENTS.

I am glad to be able to acknowledge my indebtedness to Dr. G. D. Osborne, first and foremost, for having so kindly conducted me to the finest outcrops of contorted varves in Australia, possibly, I believe, in the world; and then to Dr. Curt Teichert for plentiful encouragement, advice, and the loan of photographs; to Dr. S. W. Carey for interesting discussions; to Dr. Rosa Temko, of Perth, for assistance in the translation of many pages of Russian (Arkhanguelsky's important work).

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EXPLANATION OF PLATES.

PLATE III.

Fig. 1.—Simple slump fold in Carboniferous varves at Seaham, N.S.W. (Photo. by Dr. C. A. Matley.)

Fig. 2.—Simple "ribbon" overfold (about 1½ inches thick) affecting little more than one varve layer, at Seaham, N.S.W. (Photo. by the author.)

PLATE IV.

Fig. 1.—Simple slump fold in Pleistocene varves in Ontario, Canada. (From Wilson, 1918, Pl. XV.)

Fig. 2.—Another slump fold in the Carboniferous varves at Seaham, N.S.W., which compares closely with Fig. 1. Note simple fold (F.), ribbon structures (R.), unconformity (U.) and normal overlying varves (N.). (Photo. by the author.)

THE TEACHERS OF GEOLOGY IN AUSTRALIAN UNIVERSITIES.*

By H. S. SUMMERS.

INTRODUCTION.

I must first thank the Council of the Royal Society of New South Wales for the honour it has done me in inviting me to deliver the Clarke Memorial Lecture for 1947. There is no need for me to say anything about the man whose work we commemorate this evening, as previous lecturers have given far better accounts of the work and influence of the Rev. W. B. Clarke than I am capable of giving.

The choice of a subject for a lecture such as this is always difficult, as one must try to interest the professional geologist as well as others not so highly qualified, though extremely interested in the subject. In the present case the difficulty was accentuated by the fact that the lecturer has retired from the teaching of geology and has had his time so fully occupied with other matters at the University that no time has been devoted to either reading or research. I had almost come to the point of refusing with regret the invitation until I thought that a historical account of the earlier teachers of geology in Australia might well be of general interest. I therefore suggested the title of "A Geologist Looks Back", but found on gathering material together that there was no suitable point to end such a historical survey except at the present day, so this geologist has not only to look back, but also to look on the present. Hence I beg leave of the Council to amend the title to "The Teachers of Geology in Australian Universities".

Sydney is the oldest University, but not the oldest in teaching geology, since geology as part of Natural Science was first taught in Melbourne in 1854 by Professor McCoy, whereas in Sydney A. M. Thomson was not appointed Reader in Mineralogy and Geology until 1866. The University of Tasmania, though established before those of Queensland and Western Australia, had no properly organized teaching of geology until 1946, when the first Professor, S. W. Carey, was appointed.

It is interesting to note that the three older Universities are named after the capital city of the State—Universities of Sydney, Melbourne and Adelaide—while the three younger ones have been named after the State to which they belong—Universities of Tasmania, Queensland and Western Australia.

In all the Universities changes in the titles of the heads of the Geological Departments have taken place, but Sydney shows the greatest variety of names of Chairs, etc.

The first appointment in Sydney was that of A. M. Thomson in 1866 as Reader in Mineralogy and Geology, but the title was changed to that of Professor of Mineralogy and Geology in 1870. After Thomson's death Archibald Liversidge was appointed Professor of Geology and Mineralogy and later became, in addition, the William Hilton Hovell Lecturer in Geology and Physical Geography.

In 1882 W. J. Stephens was appointed Professor of Natural History and took over part of the work previously taught by Liversidge, and Liversidge's

* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, July 17, 1947.

Chair was renamed "Chair of Chemistry and Mineralogy". These two Professors shared the title of William Hilton Hovell Lecturer in Geology and Physical Geography. The next change was in 1890, when Stephens became Professor of Geology and Palæontology instead of Professor of Natural History and Liversidge became Professor of Chemistry. The next change took place when T. W. E. David was appointed, in 1891, Professor of Geology and Physical Geography and William Hilton Hovell Lecturer in Geology and Physical Geography. These two titles were subsequently combined, and on David's retirement the Chair was named the Edgeworth David Chair of Geology and Physical Geography and L. A. Cotton is now Edgeworth David Professor and William Hilton Hovell Lecturer in Geology and Physical Geography.

Compared with Sydney, Melbourne has been very conservative in its terminology of Chairs. Frederick McCoy was appointed in 1854 Professor of Natural Science. Though the name of the Chair was unchanged during McCoy's life, he was virtually Professor of Geology and Palæontology in the last few years of his life, all the non-geological work of the Chair of Natural Science being taken by Professors Masson and Spencer.

McCoy was succeeded by four Professors of Geology and Mineralogy—Gregory, Skeats, Summers and Hills.

In the University of Adelaide Ralph Tate was appointed Professor of Natural Science in 1875. On his death in 1901 the work in geology was divided between two lecturers, W. Howchin, Lecturer in Geology and Palæontology, and W. G. Woolnough, Lecturer in Mineralogy and Petrology. In 1904 Woolnough resigned and D. Mawson became Lecturer in Mineralogy and Petrology. In 1918 Howchin was made Honorary Professor of Geology and Palæontology, and on his retirement Douglas Mawson was made Professor of Geology and Mineralogy.

The University of Tasmania had geology as a subject for examination but there was in most years little if any teaching of the subject except during three years when the late A. N. Lewis was part-time lecturer in the subject. However, in 1946 S. W. Carey was appointed Professor of Geology.

Queensland commenced with a Lecturer in Geology and H. C. Richards was appointed in 1911, but in 1919 became Professor of Geology and Mineralogy and continued in this office until his recent death.

Western Australia commenced with a Professor as one of the Foundation Chairs and W. G. Woolnough was appointed Professor of Geology in 1912. After his retirement the Council decided not to appoint another Professor and E. de Courcy Clarke was appointed Lecturer-in-Charge of Geology but later was made Associate Professor and finally in 1930 he became Professor of Geology in the University of Western Australia.

I propose to deal with the Universities in order of age of establishment, and so will take Sydney first. In many cases, especially in the later appointments, it has been difficult to obtain all the information that one would have liked to include, and many members of the staff will not receive the notice that their position or research records would justify. To such persons I apologise.

SYDNEY.

The Act establishing the University of Sydney received the Royal Assent in 1850 and Sydney is thus the senior University in Australia. No appointment in geology was made until 1866, when A. M. Thomson was made Reader in Mineralogy and Geology.

Alexander Morrison Thomson was born in London in 1841. For a short time he attended the University of Aberdeen but soon returned to London,

where at King's College he won the Prize for Natural Philosophy. He graduated B.A. in 1861 and D.Sc. in 1867.

In 1870 the Readership was raised to the status of a Professorship and A. M. Thomson became Professor of Mineralogy and Geology. He only enjoyed the honour for a short time as he died in 1871 at the early age of thirty. Thomson had the distinction of being the first Professor of Geology in Australia because McCoy, who had held office for some years prior to Thomson's appointment to the Chair, was Professor of Natural Science.

In 1872 Archibald Liversidge was appointed Professor of Geology and Mineralogy.

Liversidge was born at Turnham Green, England, in 1847, and was educated at the Royal School of Mines, where he gained the Associateship of the School. He also trained at the Royal College of Science and at Christ's College, Cambridge. He graduated B.A. at Cambridge in 1885 and M.A. in 1887. The University of Glasgow conferred the Honorary Degree of LL.D. on Professor Liversidge. He was Scholar in Natural Science 1870-71-72 and was Demonstrator in Chemistry at the University of Cambridge in 1870.

The William Hilton Hovell Lectureship in Geology and Physical Geography was established in 1877 and Liversidge was the first Lecturer appointed.

Liversidge taught Chemistry as well as Geology and Mineralogy and in 1881 the Chair held by Liversidge was renamed Chair of Chemistry and Mineralogy. This change was made so that Liversidge could devote more time to Chemistry and the Geology was to be taken by W. J. Stephens, who was appointed Professor of Natural History in the following year. Nine years later, in 1890, a further change was made and Mineralogy was dropped from the name of the Chair and Liversidge became Professor of Chemistry and remained in this Chair until his retirement in 1908. Professor Liversidge died in England in 1927. Liversidge will long be remembered for his untiring efforts in the foundation of the Australian Association for the Advancement of Science and the part he played in helping to carry on the activities of that body. He was permanent Hon. Secretary from 1888 to 1909 and President of the Association at the meeting in Sydney in 1898. Other activities included Trusteeship of the Australian Museum, Hon. Secretary and three times President of the Royal Society of New South Wales. He was awarded the F.R.S. Liversidge was much more widely known as a chemist and mineralogist than as a geologist.

W. J. Stephens was appointed to the Chair of Natural History in 1882 and took over portion of the work previously done by Liversidge.

William John Stephens was born at Levens, Westmoreland, England, in 1829. He was educated at Haversham Grammar School, Marlborough College and Queen's College, Oxford, where he graduated B.A. in 1852 with First Class Honours in Classics and Third Class Honours in Mathematics and Physics. He was elected a Fellow and Tutor of his College. On the recommendation of Dr. Jowett, with whom he had been on friendly terms at Oxford, Stephens was appointed the first headmaster of the Sydney Grammar School, and held this position from 1856 till 1866. He then conducted a school of his own at Darlinghurst until his appointment to the Chair of Natural History in 1882. From the time of his appointment until 1888 Stephens shared with Liversidge the William Hilton Hovell Lectureship in Geology and Physical Geography, but from 1888 till his death in 1890 Stephens was the only Lecturer under this foundation.

In 1890 the name of the Chair was altered from Natural History to Geology and Palaeontology, but Stephens only held this title for a short time as he died in that same year.

Stephens, as well as being an expert in Natural History was also an excellent Classical Scholar, and during portion of the years 1883-84 between the death of

Professor Badham and the arrival of his successor, Professor W. Scott, he was Acting Professor of Classics.

To fill the vacancy caused by the death of Professor Stephens, T. W. E. David was appointed to the Chair of Geology and Physical Geography and as stated above Liversidge's title was changed from Professor of Chemistry and Mineralogy to Professor of Chemistry. David also became William Hilton Hovell Lecturer in Geology and Physical Geography.

Tannatt William Edgeworth David was born at St. Fagan's near Cardiff, Wales, in 1858. He was educated at Magdalen School and at New College, Oxford, where he graduated B.A. in 1880. He first came to Australia to join the staff of the Geological Survey of New South Wales and soon showed his wonderful capacity for research. During this period he discovered and mapped the Maitland coal seams. He left the Survey on accepting the Chair of Geology at the University.

In 1897 David was leader of the party of scientists who visited the Ellice Islands, and there supervised the boring on the Funafuti Atoll. This work was carried out under the auspices of the Royal Society. The party, and also those who worked on the material in England, were required to record observations only and not to draw deductions. Among others who accompanied David were W. G. Woolnough of Sydney and George Sweet of Melbourne. E. W. Skeats and Frederick Chapman were two of those who worked in England on the material obtained from the bore cores.

During 1907-8-9 David was on leave and took part in Shackleton's Antarctic Expedition, and was the leader of the party that located the South Magnetic Pole and also led the party that ascended Mt. Erebus. During the first world war Major David organized and was O.C. of the Australian Tunnelling Co. He served from 1916 to 1919 and as Lt.-Colonel David was Chief Geologist to the British Armies on the Western Front. He retired from the Chair in 1924 and was made Professor Emeritus in recognition of his services to the University. He retained a room at the Geological Department and actively carried on research until his last illness. He died in 1934 at the age of seventy-six. Sir Edgeworth David had a wonderful personality and made friends wherever he went. During the latter part of his life he was the acknowledged leader of geology in Australia and was respected by all his colleagues. During the long period he was associated with the University, David travelled over most of Australia and collected an enormous amount of information on the geology of Australia and he was engaged before and during his retirement in writing up this material with a view to publication. The task was so great that it was far from finished at the time of his death.

David received many honours during his life, including C.M.G. (1910), D.S.O. (1918), K.B.E. (1920). Many Universities, including Oxford and Manchester, made him Honorary D.Sc. Wales and others made him Hon. LL.D. He was elected F.R.S. in 1900. Two Australian awards were the Mueller Medal in 1900 and the Clarke Memorial Medal in 1919. He was President of Section C (Geology) of the Australian Association for the Advancement of Science in 1892 at Hobart and again in 1895 at Brisbane. He was President of the Association in 1904 at Dunedin and again in 1913 in Melbourne. The honour of being twice President of the Association is shared with no other scientist.

During his period at the University of Sydney David saw many changes in staff. In his first year he constituted the whole staff, but with increase in the number of students so the number of members of staff grew.

The first appointment was that of William Smeeth, M.A., B.E., A.R.S.M., who joined the staff in 1893. Smeeth, who received his training at the Royal School of Mines, was also Lecturer in Metallurgy. In 1897 Smeeth resigned the

Demonstratorship in Geology and in the following year W. G. Woolnough, who had graduated B.Sc. in 1898, became Demonstrator, and continued in this position until 1901, when he was appointed Lecturer in Mineralogy and Petrology at the University of Adelaide. His record is discussed under Western Australia, where he was the first Professor of Geology.

In 1902 there were four new appointments :

A. H. S. Lucas, B.Sc., as Evening Lecturer in Physiography ;
Herbert Stanley Jevons, Assistant Lecturer in Mineralogy and Petrology ;
A. J. Peterson, B.Sc. (London), Demonstrator for the Lent term ;
W. S. Dun, as Lecturer in Palæontology.

The names of Lucas and Peterson occur in the University Calendar for only one year.

H. S. Jevons remained on the staff till the end of 1904, and W. S. Dun continued as Lecturer in Palæontology until 1934.

Herbert Stanley Jevons, M.A., B.Sc., was born in England in 1875 and was educated at University College, London, and Trinity College, Cambridge. He was Demonstrator in Petrology at Cambridge during 1900-01 and was Lecturer at Sydney 1902-04. After leaving Sydney Jevons drifted more and more towards Economics and was Professor of Economics at University College, South Wales, and later at Allahabad.

In 1906 T. Griffith Taylor was Junior Demonstrator, but left in 1907 with the Shackleton Antarctic Expedition. Though Taylor did little in the teaching of geology in Australia, he has made a name for himself as a geographer. Thomas Griffith Taylor, B.A., D.Sc., B.E., was Associate Professor of Geography at the University of Sydney from 1920 to 1928 and while nominally under Professor David was virtually independent. Taylor left Sydney to become Professor of Geography at the University of Chicago from 1928-1931 and transferred from Chicago to Toronto and still holds the position of Professor of Geography at Toronto.

In 1908 during Professor David's absence in Antarctica and again in 1923 when there was shortage of staff, Dr. C. Anderson filled the breach and was appointed Temporary Lecturer in Geology. Charles Anderson graduated M.A. at the University of Edinburgh and in 1901 was appointed to take charge of the Mineralogical Department of the Australian Museum. For his work there he was awarded the D.Sc. degree by the University of Edinburgh. Dr. Anderson was Director of the Museum from 1921 to 1940, when he retired.

In 1909 W. N. Benson was appointed Junior Demonstrator. Benson did a large amount of research work in Australia, but his main teaching has been done at the University of Otago.

William Noel Benson was born in Sydney in 1885 and received his geological training in the Sydney and Cambridge Universities. He was Acting Lecturer in Geology at the University of Adelaide in 1908, Demonstrator in Sydney 1909-10. During 1910-11 as an 1851 Exhibition Scholar he studied at Cambridge University and at several European Universities. He returned to Sydney and held a Linnean Macleay Fellowship from 1914-15. He was Acting Lecturer in the University of Sydney during 1916 and was appointed Professor of Geology at the University of Otago in 1916. He was elected F.R.S. in 1941.

In 1910 A. B. Walkom joined the staff as Junior Demonstrator but most of his teaching was done at the University of Queensland (see later).

In 1911 Leo A. Cotton, who had been appointed as Demonstrator in 1908, was appointed Assistant Lecturer and has remained on the staff ever since.

W. R. Browne joined the staff as Junior Demonstrator in 1912. Records of Cotton and Browne will be discussed later.

C. E. Tilley was Junior Demonstrator in 1916 and 1919 but has done very little teaching in Australia. He had his early training in Adelaide, where he

graduated B.Sc. in 1914. He then transferred to Sydney and took his B.Sc. Sydney in 1916 with First Class Honours and the University Medal in Geology and Chemistry. He was engaged in munitions work in England from 1916 to 1919, and in 1920 was elected to the 1851 Exhibition Scholarship from Sydney. During 1920-22 he carried out research work at Cambridge, where he graduated Ph.D.

Tilley was Lecturer in Mineralogy and Petrology at Cambridge from 1928 till 1931, when he was appointed Professor of Mineralogy and Petrology. He was elected F.R.S. in 1938.

L. L. Waterhouse joined the staff in 1917 as Acting Lecturer but came on the permanent staff in 1920 and is still a member.

Lionel Lawry Waterhouse was born at West Maitland in 1885 and was educated at Sydney High School and the University of Sydney, where he graduated B.E. (Mining) in 1909.

Prior to his appointment at Sydney he spent several years as Assistant Government Geologist and Inspector of Mines in Tasmania. Here he carried on excellent work under very adverse field conditions.

Waterhouse has for many years had charge of the courses in geology for engineers, which he has built up to a high standard, and his research and teaching have been almost wholly on the side of economic geology. He was promoted to the grade of Reader in 1946.

In 1923 E. C. Andrews was appointed an Acting Lecturer during Professor David's absence.

Ernest Clayton Andrews graduated B.A. (Sydney) in 1894 and was one of David's earliest students. He was a member of the staff of the Mines Department for many years, both as Senior Geological Surveyor and Government Geologist 1920-31, when he retired. Though he was not directly connected with the teaching of the subject for long, Andrews has done a great deal of educational work in geology both by means of published research work and by means of public lectures. He was awarded the Syme Prize in 1915. Andrews was the President of the A.N.Z.A.A.S. in 1930 at Brisbane.

He was awarded the Clarke Memorial Medal in 1928, the Lyell Medal in 1931, and the Mueller Medal in 1946. Andrews led the Commonwealth delegation to the Pan-Pacific Science Congress in Java, 1929; Canada, 1933; United States, 1939. He was the Silliman Lecturer at Yale University in 1927.

In 1924 a great change took place as Sir Edgeworth David retired and Leo A. Cotton became Professor in his stead.

Leo Arthur Cotton was born at Nymagee, New South Wales, in 1883, and was educated at the Fort St. School and the University of Sydney. He graduated B.A. with First Class Honours in Mathematics in 1906 and B.Sc. with First Class Honours in Mineralogy in 1908, in which year he was appointed Demonstrator in Geology. As a Linnean Macleay Fellow he carried on research work on the tin deposits of New England during 1909-10 and returned to the staff of the University as Assistant Lecturer and Demonstrator in Geology in 1911. As might be expected from his First Class Honours in Mathematics, Cotton's tendency in his research work has been largely towards mathematical and physical interpretations of geological phenomena, and in 1920 he was awarded the degree of D.Sc., his principal thesis being "Earthquake Frequency with Special Reference to Tidal Stresses in the Lithosphere".

In 1921 Dr. Cotton was made Assistant Professor of Geology, and held this position until appointed to the Chair in 1925. Among other activities Cotton was a member of the ship's party 1907-08 of the Shackleton Antarctic Expedition. He represented his University at the First Pan-Pacific Science Congress at Honolulu in 1920 and the Third at Tokyo in 1926. He was President of Section C (Geology) of the A.A.A.S. at the Hobart meeting in 1928, where he

gave a masterly discourse on the Causes of Diastrophism. During the war period he was Chairman of the Advisory Committee of Scientific Man Power (General), Chairman of the Mineral Resources Committee, Chairman of the Australian National Research Council, and Dean of the Faculty of Science. He has been a member of the Council of the Royal Society of New South Wales for some years and was President in 1929.

One member of the staff who had served long with David and continued as a Lecturer with Cotton was W. S. Dun.

William Sutherland Dun was born at Cheltenham, Gloucestershire, in 1868 and arrived in Australia the following year. He was educated at Newington College and studied geology at the University of Sydney, first under Professor Stephens and later under Professor David. He joined the Mines Department in 1890 and was for a short time assistant in the Hunter River area to David, who was then still a member of the Geological Survey of New South Wales. In 1893 Dun became assistant to Robert Etheridge, Junr., and under his guidance became an able palæontologist. In 1902 he became part-time Lecturer in Palæontology at the University and continued to hold the position of palæontologist to the Survey and for years was Honorary Palæontologist to the Australian Museum.

For many years W. S. Dun was the leader in his subject, especially in the Upper Palæozoic fauna of Australia, but more particularly that of New South Wales. His greatest interest was in the Lamellibranchs and the Brachiopods. He was President of the Linnean Society of New South Wales in 1913. He became a member of the Royal Society of New South Wales in 1908 and for many years was a member of the Council and was President in 1918. W. S. Dun died in 1934, in the same year as his friend and colleague Sir Edgeworth David, so that geologists and others, not only in New South Wales but in the whole of Australia, lost in the one year two men whom all felt honoured to call their friends.

Of the present members of the staff, W. R. Browne is the next senior to Professor Cotton.

William Rowan Browne was born at Lislea, Co. Derry, Ireland, in 1884, and received his early training in Ireland, but came to Australia and entered the University of Sydney, where he graduated B.Sc. in 1910 and D.Sc. in 1922. He first joined the staff as Junior Demonstrator in 1912, but the following year was appointed Assistant Lecturer and Demonstrator, and held this post until 1923, when he was appointed Assistant Professor. The title of Reader in Geology, which had been in abeyance since the time of A. M. Thomson, was again brought into use, and in 1939 W. R. Browne relinquished the title of Assistant Professor to become Reader in Geology in the University of Sydney.

From 1935 to 1939 Dr. Browne was relieved from his University duties to undertake the work of editing and preparing for publication the mass of MSS. which Sir Edgeworth David had accumulated on the geology of Australia, and at present is in England making arrangements for the publication of this important work. Dr. Browne has been twice President of the Linnean Society of New South Wales, in 1928 and again in 1944, and President of the Royal Society of New South Wales in 1932.

G. D. Osborne was first appointed to the staff as a Demonstrator in 1922, and but for one year has remained a member ever since.

George Davenport Osborne was born in 1899 at Sydney and was educated at Sydney High School and the University of Sydney, where he graduated B.Sc. in 1921 with First Class Honours and the University Medal. He was a Demonstrator from 1922 to 1924, when he was elected a Linnean Macleay Fellow in Geology. He held this Fellowship during 1925, but returned in 1926 to the

University as Lecturer and Demonstrator. In 1929 he was awarded the D.Sc. degree for research work, which was largely in connection with the structural features of the deposits of the Hunter River Valley.

In 1930 and again in 1938 Osborne was granted leave and went to England, where he gained the degree of Ph.D. in Mineralogy and Petrology at the University of Cambridge. Osborne was appointed Research Associate at Harvard University in 1939 and subsequently, with the award of a Carnegie Travelling Grant, visited many parts of Canada and the United States.

Dr. Osborne has had several years on the Council of the Royal Society of New South Wales, and was President in 1944. He has carried out extensive research on the Upper Palaeozoic rocks of New South Wales with special stress on structural details.

Ida A. Brown joined the staff in the same year as Dr. Osborne, but has not had such continuous service.

Ida Alison Brown was born in 1900 in Sydney and was educated at Fort St. Girl's High School and Sydney University, where she gained her B.Sc. in 1922 with Honours in Mathematics and Geology and the University Medal in Geology. She was appointed Demonstrator in 1922. From 1927-1933 she held a Linnean Macleay Fellowship and carried out extensive field work in rugged country along the South Coast area of New South Wales. Her petrological studies showed that some rare rock types were present in the area. She was awarded the degree of D.Sc. in 1932 for this work.

Ida Brown was again Demonstrator in 1934 and was appointed Lecturer in Palaeontology in 1935 in succession to W. S. Dun, and soon showed that she could change from a perfectly good petrologist to an equally able palaeontologist.

Among the Demonstrators who have either at times been Acting Lecturers or have been on the staff for some years, the following may be mentioned :

Catherine Drummond Smith, B.Sc. 1911 (now Mrs. F. S. Cotton), was on the staff from 1912 till 1919.

Dorothy K. Powell, B.Sc. 1920, was a Demonstrator from 1920 until 1933, and was Acting Lecturer during Dr. Osborne's absence in 1931.

Florrie Quodling was first appointed a Demonstrator in 1924. She graduated in 1924 and is still a member of the staff. Miss Quodling was Acting Lecturer during W. R. Browne's absence in 1936-39, and some years ago was appointed Lecturer.

Germaine Joplin graduated B.Sc. in 1930 with First Class Honours and the University Medal and was appointed Curator of the Museum in 1931. In 1933 Miss Joplin was awarded a Junior Fellowship of the International Federation of University Women and studied at Cambridge, where she was awarded the Ph.D. degree for research work carried out in England. On her return she was Acting Lecturer from 1936 to 1939, and was in 1941 awarded a Linnean Macleay Fellowship in Geology. She carried out extensive field work and the necessary laboratory work on the igneous and metamorphic rocks of the districts around Cooma, Albury and other parts of New South Wales. Dr. Joplin at present holds a Teaching Fellowship at the University of Sydney.

J. A. Dulhunty graduated B.Sc. in 1938 with First Class Honours in Geology and was a Demonstrator during 1938-39. In 1940 he was elected a Linnean Macleay Fellow in Geology. He carried out extensive research into the occurrence and uses of torbanite and was awarded the degree of D.Sc. for this work. He has been on the Council of the Royal Society for some years and is the President for 1947.

In 1947 A. V. Jopling, B.E., B.Sc., was appointed Teaching Fellow in Geology.

Other graduates who have acted as Demonstrators and/or Curators include :

Fanny Cohen, B.A. 1908, B.Sc. 1909 : Demonstrator 1909-11.

S. J. G. Davis, B.Sc., Demonstrator in 1913.

Olga Marian Pauss, B.A. 1912 (now Mrs. W. R. Browne). First Curator, 1913.

E. J. Kenny, who for many years was a member of the Geological Survey of New South Wales and later Assistant Under Secretary for Mines, was Demonstrator in 1917.

Doris Stilwell, B.Sc., was Curator for several years from 1917.

Harold Yates, B.Sc., was a Demonstrator in 1919. He has for many years been teaching Geology at the Ballarat School of Mines. He was awarded the degree of M.Sc. for research work in the Yass district.

Elaine Shepherdson, B.Sc. (now Mrs. Wilshire), Curator 1923-28.

Heather Drummond, B.Sc., Demonstrator 1925.

Jeanette E. Johnson, B.Sc. (now Mrs. Park), Curator 1929.

Alma G. Culey, M.Sc., became a Demonstrator in 1931 and was Acting Curator during Miss Joplin's leave.

Una A. Pickard, B.Sc. (Mrs. J. Black), Demonstrator 1935-37.

In 1938 Marion Breckenridge, B.Sc., was appointed Acting Curator, later Curator. The position is now held by Mabel Milthorpe, B.Sc.

A. J. Lambeth, B.Sc., was Demonstrator in 1939.

Joan Johnson, B.Sc. (now Mrs. D. G. Moye), Demonstrator in 1940.

Joan M. Crockford, M.Sc. (Mrs. G. Beattie), was appointed Demonstrator in 1942.

Mrs. J. Windridge, B.Sc., has been a Demonstrator since 1945.

Helen McRoberts, B.Sc., was Demonstrator in 1946.

Beryl Scott, B.Sc., and B. Champion, B.Sc., have been appointed Demonstrators for 1947.

The New England University College was established at Armidale in 1938 and A. H. Voisey was appointed in 1939 as Lecturer in Geology and Geography.

Alan Heywood Voisey graduated B.Sc. from the University of Sydney in 1933 with First Class Honours and the University Medal in Economic Geology, and M.Sc. in 1936. For several years he was a geologist attached to the Northern Territory section of the Aerial, Geological and Geophysical Survey of Northern Australia. In 1937 Voisey was elected a Linnean Macleay Fellow and continued the research work which he had begun while a student. His principal interest was in the relationship of the Carboniferous and Permian in north central New South Wales and their correlation with rocks of somewhat similar age in other parts of Australia. He visited Tasmania in 1938 to get first-hand knowledge of the Upper Palæozoic deposits of that State. For his work on the Upper Palæozoic Systems he was awarded the degree of D.Sc. in 1944.

Elizabeth M. Basnett (Mrs. A. Robbins), after a brilliant academic career, graduated B.Sc. in 1939 and M.Sc. in 1941. She was appointed Demonstrator at Armidale in 1941, and lectured there in petrology for five years. She was succeeded in 1946 by Miss Margaret J. Colditz, M.Sc., who was Acting Lecturer for a period of eighteen months.

MELBOURNE.

The Act to establish the University of Melbourne was assented to by the Governor in 1853 and the first Council was appointed in that year. The Council decided to ask a committee in England to select four Professors, and one of those chosen, Frederick McCoy, became the Professor of Natural Science.

Frederick McCoy was born in Dublin in 1823. He studied medicine first at Dublin and subsequently at Cambridge. Though he apparently qualified,

he was too young to be admitted to practice, and being offered a post as palæontologist in connection with the Geological Map of Ireland he drifted right away from Medicine and does not appear to have been admitted to any degree or to practice in medicine. As a result of his work in Ireland he published two large volumes containing descriptions with drawings of many new varieties of fossils. One volume was devoted to the Carboniferous Limestone Fossils of Ireland and the other to the Silurian Fossils of Ireland. Adam Sedgwick asked him to arrange the collections of fossils in the Woodwardian Museum at Cambridge and he was engaged on this work from 1846 till 1854. For a short time McCoy joined the English Geological Survey but left in 1850 to take the Chair of Geology and Mineralogy at the Queen's College, Belfast. He still carried on the work at the Woodwardian Museum during his vacations and the results of his work were published under the title of "British Palæozoic Rocks and Fossils". In 1855 McCoy commenced work in Melbourne as the Professor of Natural Science.

The foundation stone of the University was laid in 1854 but the buildings were not declared open until the 3rd October, 1855. The first Matriculation Ceremony took place and the first lectures were delivered in the Exhibition Building, but in the latter part of the year the work was transferred to the University.

At the time of his appointment McCoy held no University degree, but while in England on six months' leave in 1886 he was awarded the honorary degree of Sc.D. by the University of Cambridge and the M.A. degree by the Royal University of Ireland. On his return to Melbourne McCoy was admitted *ad eundem gradum* to the degree of D.Sc., being the first recipient of that degree in the University of Melbourne. Subsequently he was admitted *ad eundem gradum* to the degree of M.A.

During McCoy's absence the Rev. A. W. Crosswell, M.A., acted as his *locum tenens*. A. W. Crosswell had trained under McCoy and for some years was a member of the Board of Examiners in Natural Science.

Up till 1885 McCoy was expected to conduct three courses, one for each year of the Arts course. In the first year the subjects were Chemistry, Mineralogy and Botany, in the second year Comparative Anatomy and Zoology, and Geology and Palæontology were the subjects of the third year. The Chemistry had for some time been taken by John D. Kirkland, first as a Lecturer and later as a Professor of Chemistry.

In 1885 the Council decided that the subjects of the Chair of Natural Science were too broad and decided that Chemistry should be solely taught by Professor David Orme Masson, who was appointed to the Chair of Chemistry in that year. As it had been decided to establish a Chair of Biology, to which Walter Baldwin Spencer was appointed the following year, the Council further decided that Comparative Anatomy and Zoology should be divided between the Professors of Natural Science and Biology and that McCoy should retain the teaching of Geology and Palæontology. This arrangement did not last long, as in 1887 the regulation governing the degree of Bachelor of Science was passed and the grouping of subjects was altered. Natural Science was dropped from the Arts course and Geology, Mineralogy and Palæontology became subjects of the second and third years of the Science course. McCoy carried on nominally as Professor of Natural Science but actually as Professor of Geology until his death in 1899. Frederick McCoy founded the Museum of Natural History, and this was housed in the building now forming part of Union House. Later the bulk of the material was transferred to the National Museum in Swanston Street. McCoy was the Director of the Museum for forty-five years. In addition to his other duties McCoy acted as Palæontologist to the Geological Survey of Victoria and determined a large number of fossils collected by members of the Survey. He thus

helped to determine the ages and sequence of the various formations. The *Prodromus of the Palæontology of Victoria* is still a standard book of reference, as is also the *Prodromus of the Zoology of Victoria*. McCoy received many honours, among which may be mentioned F.G.S. (1852), F.R.S. (1880), C.M.G. (1886), K.C.M.G. (1891).

During McCoy's last illness and for the period between his death and the arrival of Professor Gregory the work of the Department was divided between T. S. Hall and G. B. Pritchard, both of whom had been taught by McCoy.

Thomas Sergeant Hall, M.A., D.Sc., was for many years the leading authority in Australia on the Graptolites. He became interested in this group while in charge of the Castlemaine School of Mines and after his appointment to the staff of the Biology School under Professor Spencer he continued his keen interest in this group of fossils and also carried on research on the marine Tertiary deposits of south-eastern Australia.

George Baxter Pritchard was for many years in charge of Geology, Assaying and Metallurgy at the Working Men's College (now the Melbourne Technical College). He was also attached for some time to the Chemistry School at the University as part-time Lecturer in Metallurgy. Pritchard's main interest was in the Mollusca, both Recent and of Tertiary age, and either as sole author or in collaboration with T. S. Hall or others, published numerous papers on Tertiary stratigraphy and palæontology.

The Chair of Natural Science having been changed to that of Geology and Mineralogy, J. W. Gregory in 1900 became the first Professor of Geology and Mineralogy in the University of Melbourne.

John Walter Gregory was born in London in 1864. He was educated at Stepney Grammar School and then entered the wool business in 1879 and remained in this occupation until in 1887 he was appointed an assistant in the Geological Department of the British Museum. While holding this post he found time to study Geology at the University of London and graduated B.Sc. in 1891 and D.Sc. in 1893. He remained with the British Museum until 1899 but while still on the staff spent some time in the Rocky Mountains and the Great Basin of the western States. In 1892-93 he was in British East Africa, the result of his work there being published as "The Great Rift Valley". In 1896 he accompanied Sir Martin Conway's expedition across Spitzbergen. Gregory spent less than five years in Australia but managed in that time to visit most parts of Victoria as well as to travel in other States. He took a party of students to central Australia during the long vacation 1901-02 and subsequently published "The Dead Heart of Australia". Though his views on the origin of the waters of the Great Artesian Basin are not accepted, as a result of his statements, opponents to his views brought to light far more information about this area than would probably have been obtained otherwise. In addition to his work as Professor he was freed part time from 1901 to become Director of the Geological Survey of Victoria and D. J. Mahony was appointed to relieve him of some of his duties at the University. Gregory left Victoria at the end of the second term in 1904 to take the Professorship of Geology at the University of Glasgow and Mahony carried on the work of the Department till the arrival of E. W. Skeats in 1905.

After leaving Australia, Gregory still found time to travel, and visited and explored Cyrenaica in 1908, Southern Angola in 1913, Chinese Tibet in 1922. In 1932 J. W. Gregory led an expedition to Peru and on the 2nd of June of that year was accidentally drowned in Urubamba River.

Daniel James Mahony, M.Sc. (Melb.), commenced an engineering course at the University, but due to the influence of Gregory he transferred to Science. Mahony joined the Geological Survey of Victoria as petrologist in 1906. He served in World War I with the Royal Artillery.

In 1931 Mahony was appointed Director of the National Museum. He died in 1946.

E. W. Skeats was appointed to the Chair of Geology and Mineralogy after the resignation of Gregory and arrived in Melbourne in February, 1905.

Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., was born at Southampton in 1875. He was educated at Handel College and Hartley College, Southampton, and at the Royal College of Science, South Kensington, where he gained a First Class Associateship in Chemistry in 1896 and in Geology in 1897. He graduated B.Sc. London in 1899 and D.Sc. in 1902, his principal thesis dealing with the origin of the dolomites of the Tyrol. Before his appointment to Melbourne Skeats was a Demonstrator at the Royal College of Science under Professor Judd. When Skeats took up his duties in Melbourne he was entirely responsible for the teaching of Geology and Mineralogy, but had an exceptionally able technical assistant in the late H. J. Grayson, who is more generally known for his fine rulings and the construction of a machine for ruling diffraction gratings. The Geology Department was at first housed in part of the original building of the University, but in 1907 it was transferred to a new building which had been erected to take Geology, Mining and Metallurgy. The amount granted for this building was insufficient and it was never very satisfactory. After the first world war extra temporary accommodation in ex-army huts had to be provided. As both Engineering, which adjoined the Geology Building, and Metallurgy required room for expansion, it was decided to provide a new Geology School, and this was officially opened in 1927.

With the growth of the School this building is no longer large enough and additions are being built at the present time.

Professor Skeats saw great changes during his long tenure of office from 1905 to 1940. When he first took up his duties Geology could be taken by second and third year Science students, second year Civil and Mining Engineers and third year Mining Engineers, and the Professor had to give lectures over one term in Physical Geography as part of a subject called Natural Science taken in the course for the Diploma of Education. Subsequently the Science Regulations were amended and Geology Parts I, II and III became subjects of the three years of that course. Natural Science ceased to be a subject of the Diploma of Education. Other courses taken now are Agricultural Geology, Geology Part I (Engineering Course), Geology Part I (Architecture Course) and Mining Geology. Skeats held many positions both within and without the University. He was Dean of the Faculty of Science, 1910-15; President of the Professorial Board, 1922-24; President Section C (Geology) A.A.A.S. in 1909 at Brisbane; and President of the Royal Society of Victoria, 1912-14. Professor Skeats was invited to deliver the first Clarke Memorial Lecture and later the first Edgeworth David Lecture. He retired in February, 1941, and in recognition of his services to the University he was elected Professor Emeritus of Geology.

Skeats built up a wonderful reputation for the School of Geology, and students who trained under him are to be found in important positions in many lands.

In 1906 two Caroline Kay Scholarships were first open to competition. These Scholarships were teaching Scholarships and had a tenure of two years. One of these was assigned to Geology and H. S. Summers was the first holder of a Caroline Kay Scholarship in Geology. This afforded some relief to Skeats, as Summers took over the lectures in Mineralogy and Petrology to the senior students. Caroline Kay Scholars who followed were required to demonstrate only. The names of the Scholars, in order of appointment, are as follows: H. S. Summers, D.Sc.; H. C. Richards, D.Sc., late Professor of Geology, University of Queensland; E. O. Thiele (now Sir Edmund Teale, D.Sc.), who has spent most of his life on geological surveys under the Colonial Institute;

F. L. Stillwell, D.Sc., now in charge of the Mineragraphy Section of the C.S.I.R. in Melbourne; M. Morris, M.Sc.; N. R. Junner, D.Sc., Director of the Geological Survey of the Gold Coast; C. A. Hoadley, M.Sc., who until his recent death was Principal of the Footscray Technical School; P. G. Towl, M.Sc., who was killed in action in World War I; and the last holder was Kathleen McInerny, M.Sc. (now Sherrard). In 1920 the University Council decided that the post of Assistant Lecturer would be established, provided that the Caroline Kay Scholarship in Geology was surrendered. The Scholarship is now the Caroline Kay Scholarship in Botany. Kathleen McInerny was appointed to the position of Assistant Lecturer and took over the lecturing on Building Stones and Road-Metals to Engineering and Architecture students.

Kathleen McInerny was admitted to the degree of Bachelor of Science in 1918 and of Master of Science in 1921. Miss McInerny was the first woman to graduate in Science at Melbourne, with Geology as a major subject. She was awarded the Caroline Kay Scholarship in 1918 and in 1920 became Assistant Lecturer in Geology. During 1929 Miss McInerny was granted leave of absence to visit England.

In 1920 Bertha Keastland graduated B.Sc. with Geology as her major subject and was admitted to the degree of M.Sc. in 1922. Miss Keastland was for many years attached to the Teachers' College, Melbourne, where she was in charge of students taking Geology at the University. During this period Miss Keastland frequently acted as part-time Demonstrator in Geology at the University.

In 1921 Frederick Chapman was appointed part-time Lecturer in Palæontology.

Frederick Chapman was born in London in 1864. For some years he was assistant to Professor Judd at the Royal College of Science. During this period he became intensely interested in microorganisms, particularly, and in any forms of fossils generally. His book "The Foraminifera" was for long a leading textbook on this group of fossils. On the recommendation of Professor Gregory he was appointed Palæontologist to the National Museum, Victoria, in 1902. During his stay at this institution he arranged and catalogued the collections and in addition figured and described a very large number of forms. From 1921 F. Chapman lectured and demonstrated in Palæontology to students taking Geology, Parts II and III. In 1927 Chapman transferred from the State to the Commonwealth, but retained his room at the National Museum and also continued to lecture at the University. He retired from the position of Commonwealth Palæontologist in 1935. He died in 1943.

In 1921 another important appointment was made. F. A. Singleton was appointed Lecturer in Agricultural Geology and Curator of the Museum.

Frederick Alexander Singleton was born in 1897 and was educated at the Melbourne Church of England Grammar School and the University of Melbourne. He was appointed a Lecturer in 1921 but two years later was made Senior Lecturer.

Singleton graduated B.Sc. in 1919, M.Sc. in 1921 and D.Sc. in 1940, in which year he also won the Syme Prize for Scientific Research. During Professor Hills' absence in England in 1946 Singleton was Acting Professor. In the same year Singleton was awarded the well-merited honour of being made Associate Professor of Geology, but unfortunately did not live long to enjoy the distinction and his death this year while still comparatively young robbed the University of an exceedingly zealous and efficient officer. Throughout his connection with the staff of the Geological Department Singleton was in charge of the Museum and the standard of his work in this connection is best shown by the paragraph in the report of Messrs. Markham and Richards to the Carnegie Corporation of New York on Museums and Art Galleries in Australia. On page 39 of this

report the following appears: "The Museum at the Geology School of the University of Melbourne has the best labelled and displayed geological collection in Australia and as a means of serving the purposes of the University, must rank very highly indeed in comparison with similar Museums throughout the world."

After the retirement of F. Chapman, Singleton had the work of lecturing in Palæontology added to his other work and until his death took this portion of the work in Geology Parts I, II and III. He also lectured to Part III on Australian Tertiary stratigraphy and on Fossil Man. Singleton was one of the leading palæontologists in Australia and was the Australian authority on the Tertiary Mollusca.

In 1923 H. B. Hauser, M.Sc., who had been a Junior Demonstrator, was raised to Senior Demonstrator and J. S. Mann, while still carrying on as Senior Technical Assistant, was given the additional rank of Demonstrator.

For several years from 1929 Ann Nicholls (now Mrs. Marshall) was a Demonstrator in Geology.

Ann Nicholls graduated B.Sc. in 1929 and M.Sc. in 1930. She was not only a Demonstrator in Geology but was also Tutor and later Assistant Lecturer in Economic Geography in the School of Commerce.

Miss Nicholls spent over a year in America studying Geography, first with T. Griffith Taylor at Toronto, and later in California. She also carried out research on soils in the Colac area in conjunction with Professor Wadham and Mr. Leeper.

In 1932 the Assistant Lectureship that K. McNerny had held was raised to a Lectureship and E. S. Hills was appointed to the post.

Four other men who were Junior Demonstrators for limited periods but who have since risen to high positions are:

Charles Fenner, D.Sc., who was later Principal of the Ballarat School of Mines and Lecturer in Geology, and is now Director of Education in South Australia.

Charles Wilson, D.Sc., who until his recent death was Director of the Geological Survey of Nigeria.

Arthur Lennox Conlon, D.Sc., and John Alexander Dunn, D.Sc., who have both recently retired from the Indian Geological Survey. Both rose to the position of Superintendent and both for some time were in charge of the Museum at Calcutta, which position also carried the post of Professor of Geology at the University of Calcutta.

With the resignation of Skeats in 1941, H. S. Summers was appointed Professor, but owing to age limitations only held the position for a very short period.

Herbert St. John Summers was born at Benalla in 1876 and was educated at the Carlton Grammar School (now extinct) and the University of Melbourne. There was a considerable gap between the time he qualified for Matriculation in 1890 and the time he entered the University in 1903. This time was largely spent in teaching in Queensland and Victoria. Summers graduated B.Sc. in 1905, M.Sc. in 1907 and D.Sc. in 1913. He first became a member of the staff as a Caroline Kay Scholar in 1906. He was appointed Assistant Lecturer and Demonstrator in Geology in 1909. This position was subsequently reclassified as Senior Lecturer. Several times during Skeats' absence Summers was appointed Acting Professor. In 1921 he became Associate Professor of Geology and in 1941 became Professor of Geology and Mineralogy, but resigned in 1944. Summers was a member of the University Council for twelve years from 1921 to 1935; President of the Royal Society of Victoria in 1931-32; President, Section C (Geology) A.A.A.S., Sydney, 1932.

When Summers became Professor some changes in the staff had to be made, but such changes were kept to a minimum so that his successor should have a freer hand. Previously Skeats had lectured on Mining Geology, so A. B. Edwards, of C.S.I.R., with the concurrence of Sir David Rivett, was appointed part-time Lecturer in Economic Geology.

Austin Burton Edwards graduated B.Sc. in 1930 at the University of Melbourne and showed even during his course evidence of the research spirit. He won an 1851 Science Research Scholarship and studied at the Royal College of Science and gained the Ph.D. degree at the University of London. He returned to Australia to join the staff of the C.S.I.R. in the Mineragraphy Section, which is housed in the Geological Department of the University. While carrying out mineragraphic investigations he found time to do extensive research work in General and Economic Geology. For his research work he was awarded the D.Sc. degree of Melbourne. He shared the Syme Prize in 1937.

Mention may be made here of Dr. F. L. Stillwell, who for many years has given several lectures per annum on subjects on which he is an expert to third year Science and fourth year Mining Engineering students.

Stillwell made a special study of Broken Hill, Bendigo and Kalgoorlie mining fields, but his major work has been the examination of ore and gangue minerals by reflected light on polished surfaces of the minerals. He has just returned from Fiji, having been asked to report on a microscopic examination of the ores with special reference to the tellurides. Stillwell graduated B.Sc. 1911, M.Sc. 1913, D.Sc. 1916. He was the Syme Prize winner for 1919.

Sylvia Bosselman was Demonstrator in Geology during 1939-40. Miss Bosselman (now Mrs. Whincup) obtained First Class Honours and the Exhibition in Geology right through her course. She is now Mineralogist and Petrologist at the National Museum, Melbourne.

In 1944 E. S. Hills was appointed Professor of Geology and Mineralogy.

Edwin Sherbon Hills was born in 1906 at Melbourne. He was educated at the University High School and the Universities of Melbourne and London. During his course at Melbourne he gained First Class Honours and first place with the Exhibition in Geology Parts I, II and III. He was placed first with First Class Honours in the M.Sc. Examination and won the Final Honours Scholarship and the Kernot Research Scholarship. He also held a Howitt Scholarship during 1928.

He graduated B.Sc. in 1928 and M.Sc. in 1929, D.Sc. in 1935. He acted as a Demonstrator for a short time in 1929 but being awarded an 1851 Scholarship went to London, where he won the Ph.D. degree. He was then offered a Lectureship in Geology at Melbourne and accepted the post and returned to Australia in 1932. In 1940 he shared the Syme Prize. In 1941 he was made a Senior Lecturer and an Associate Professor in 1942.

Hills is on the Council of the Royal Society of Victoria. He is Dean of the Faculty of Science and is the President Elect of Section P (Geography) at the A.N.Z.A.A.S. to be held in August of this year.

On the appointment of Hills to the Chair quite a number of changes were made in the staffing of the Department.

In 1944 the position of Senior Lecturer in Mineralogy and Petrology was filled by the appointment of C. M. Tattam, who commenced duties in 1945.

Charles Maurice Tattam was born in 1903 at Caulfield, and was educated at Essendon High School and the Universities of Melbourne and London and the Colorado School of Mines. He graduated B.Sc. in 1924 and qualified for the M.Sc. degree in 1925, but has never taken it out. In 1926 he went to the Royal College of Science and there gained the Ph.D., London. For some years he was on the staff of the Geological Survey of Nigeria and while on this staff he was given leave of absence on being awarded a Commonwealth (U.S.A.) Fellowship.

He took a course of geophysics at the Colorado School of Mines, where he was awarded the Sc.D. degree. He left the Survey to accept the Senior Lectureship at Melbourne.

Howard Bolitho Hauser was educated at the University High School and the University of Melbourne, where he graduated B.Sc. in 1920 and M.Sc. in 1924. He was appointed a Demonstrator in 1920 but was allowed leave in the latter part of the year to take a temporary Lectureship at the University of Western Australia, the vacancy having been caused by the resignation of Marcel Aourousseau. He became a Senior Demonstrator in 1923 and on the appointment of Hills to the Chair he was made a Lecturer, his principal duties being lectures and demonstrations to classes in practical work.

George Baker, M.Sc., was born in Coventry, England, in 1908 and received his early education there. He came to Australia in 1925 and immediately got a position as junior assistant in the Geology School. After some time, as he had shown an aptitude for Geology, he was given time off to take the Science course and graduated B.Sc. in 1933. While still classed as a Technical Assistant he was appointed Tutor to Evening Students. He was so successful in this work that in 1945 he was made Lecturer and his principal duties are to lecture to evening students and to take charge of their practical work. He has done excellent research work and in 1935 gained the M.Sc. degree by research and in 1944 shared the Syme Prize for Scientific Research. He has always actively participated in the work of the Museum and at present is acting as Curator.

A. J. Gaskin was appointed a Lecturer in 1945. Arthur John Gaskin was educated at the University High School and the University of Melbourne. He graduated B.Sc. in 1940 and M.Sc. in 1941. Gaskin was a Demonstrator in 1941; then joined the C.S.I.R. laboratories at Fishermen's Bend, but returned to the University in 1945.

In 1945 Beryl Langham, B.Sc., who had previously been a Demonstrator, was appointed Research Assistant to Professor Hills and this was the first appointment of this type in the Geology Department, Melbourne.

Owing to the death of Associate Professor Singleton, a vacancy was caused on the staff, and this was filled by the appointment of Curt Teichert as Senior Lecturer in Palaeontology. Teichert holds the degree of Ph.D. of Königsberg and D.Sc. of Western Australia. He is an outstanding palaeontologist and was a Research Fellow for some time in the University of Western Australia, where he carried out some excellent work. He transferred to the Geological Survey of Victoria in 1916 as Assistant Government Geologist, but accepted the University post and commenced duties on the 1st of July, 1947.

ADELAIDE.

The University was established in 1874 and one of the Foundation Chairs was that of Natural Science.

In 1875 Ralph Tate was appointed to the Elder Professorship of Natural Science and was the sole member of the staff of this Department until his death in 1901. Assistant Examiners were appointed at times and J. Denmant, State School Inspector, Victoria, acted as Assistant Examiner in Geology on several occasions.

Ralph Tate was born at Alnwick, Northumberland, in 1840. He studied at the London School of Mines and taught at the London Polytechnic and at Mining Schools in Bristol and in Ireland. In 1864 he was made a Fellow of the Geological Society and appointed Curator of the Society's Museum. He was awarded the Murchison Medal in 1874 and next year took up his appointment in Adelaide. During his tenure of office he did a great deal to advance our knowledge of Geology, Botany and Zoology. He soon became an authority on the Tertiary palaeontology and stratigraphy of south-eastern Australia and figured

and described a large number of fossils from the Tertiary of Aldinga, South Australia; Muddy Creek and Mornington, Victoria; and Table Cape in Tasmania. He published many papers, principally in the *Proceedings of the Royal Society of South Australia*. In several papers J. Dennant was joint author. He was a member of the Horn Expedition to central Australia in 1894 and contributed to the scientific results of that expedition. Tate founded the Adelaide Philosophical Society. He was the first President of the Royal Society of South Australia. He was President of Section D (Biology) at the first meeting of the A.A.A.S. in 1888 in Sydney, and President of Section C (Geology) in 1900 in Melbourne.

Tate was President of the Association at the meeting held in Adelaide in 1893, and his presidential address dealt with a Century of Geological Progress in Australia. It is difficult for a palæontologist or botanist to do any work in south-eastern Australia without having to look up Tate's views on the matter under investigation. During 1901, the year in which Tate died, the Council of the University divided the work of the Department as follows: Botany, E. L. Benham; Elementary Geology, J. D. Iliffe, B.Sc.; Advanced Geology and Mineralogy, I. H. Boas, B.Sc.; and Palæontology, W. Howchin, F.G.S. J. D. Iliffe graduated B.Sc. in 1899 at Adelaide. Isaac Herbert Boas was born in Adelaide in 1878 and graduated B.Sc. in 1899 and in Western Australia graduated M.Sc. in 1916. For some years up to his recent retirement Boas was head of the Forest Products Laboratory of the C.S.I.R. in Melbourne.

The University Council decided not to make a fresh appointment of a Professor but to divide the geological work between two Lecturers, and in 1902 Walter Howchin was appointed Lecturer in Geology and Palæontology and W. G. Woolnough Lecturer in Mineralogy and Petrology. Of these two, W. G. Woolnough is dealt with under the University of Western Australia, of which he was the first Professor of Geology.

Walter Howchin was born at Norwich in England in 1845 and was educated at the Academy, King's Lynn. Howchin was ordained a minister of the Primitive Methodist Church in 1865, but being more interested in geology than theology resigned from the ministry in 1880. He came to Australia in 1881 and was Lecturer in Mineralogy at the South Australian School of Mines from 1899 to 1904.

In 1902 he became Lecturer in Geology and Palæontology at the University of Adelaide. In recognition of the high standard of his work the Council of the University in 1918 gave him the title of Honorary Professor. He resigned from the staff in 1920 but the Council asked him to retain the title of Honorary Professor.

Howchin was at first better known as a palæontologist and published many papers dealing with this branch of geology. His later published work, however, showed that he had a wide knowledge of general geology and his presidential address to Section C (Geology) A.A.A.S. in Melbourne in 1913 was a masterly presentation of the physiography of South Australia. In recognition of his services to geology Howchin received the Clarke Memorial Medal in 1907 and the Mueller Medal in 1913. He was also the first to receive the Sir Joseph Verco Medal, which was awarded to him in 1929. Walter Howchin died in 1937 at the age of ninety-two.

W. G. Woolnough resigned the Lectureship in Mineralogy and Petrology in 1904 and Douglas Mawson was appointed to the vacancy.

Douglas Mawson was born in 1882 at Bradford in Yorkshire. He received his higher education at the University of Sydney, where he graduated B.E. (Mining Engineering) in 1901 and B.Sc. in 1902. In 1903 Mawson undertook geological exploration of New Hebrides and in 1905 he took up his duties at the University of Adelaide. He continued as Lecturer in Mineralogy and Petrology

until 1920, when on the retirement of Professor Howchin the two positions were combined and Mawson became Professor of Geology and Mineralogy, a position which he still holds. During 1907-08 Mawson was a member of Shackleton's Antarctic Expedition and in 1907 W. N. Benson took over his duties in Adelaide. While in the Antarctic, Mawson was with the party that fixed the position of the South Magnetic Pole and also took part in the ascent of Mt. Erebus.

In 1909 he was awarded the degree of D.Sc. (Adelaide) largely for research work dealing with the Broken Hill Mining Field.

Mawson then set about the organization of the Australian Antarctic Expedition, of which he was the leader. Professors David and Masson gave him much help in stimulating interest in this venture. Mawson was absent from 1911 to 1914, though some of the party returned earlier. During 1914-15 F. L. Stillwell was Acting Lecturer. Stillwell had accompanied Mawson to the South, but was one of those who returned early. In 1914 Mawson was knighted as a recognition of his successful leadership of an Antarctic Expedition. Shortly after the outbreak of the first world war Mawson was granted leave and went to England, where his services were utilized in the production of munitions. He was given the temporary rank of Hon. Major. In 1917 E. O. Teale was appointed Acting Lecturer. In 1920 Mawson was awarded the O.B.E.

Sir Douglas Mawson was the leader of the British, Australian and New Zealand Antarctic Expedition which during parts of 1929-31 explored the Kerguelen Island group and carried out extensive hydrographic surveys in the Australian Quadrant. Mawson received many medals in recognition of his explorations, including the R.G.S. Antarctic Medal in 1909, the R.G.S. Founder's Medal in 1915 and the King's Polar Medal with two bars.

In 1930 he was awarded the Mueller Medal and in the same year the University of Tasmania conferred the degree of D.Sc. on Mawson as a mark of appreciation of the work he had done in Antarctica. Notwithstanding his frequent absences abroad, Mawson found time to carry out original work on many parts of South Australia. He has published many papers, chiefly in the *Proceedings of the Royal Society of South Australia*. Mawson was President of Section E (Geography-History) in 1921 at the Hobart-Melbourne meeting and President of Section C (Geology) of the A.A.A.S. in 1926 at the Perth meeting, and President of the Association in 1935 in Melbourne, where he gave a full history of exploration in Antarctica under the title "The Unveiling of Antarctica".

Shortly after Mawson was elected Professor in Adelaide, C. T. Madigan was appointed Lecturer in Geology. This was in 1922, and Madigan still held the position at the time of his death in the early part of this year.

Cecil Thomas Madigan was born in 1889 at Renmark, South Australia. He was educated at the Universities of Adelaide and Oxford. In 1910 he graduated B.Sc. (Adelaide) but surrendered this degree in 1932 to receive instead the degree of B.E. He was selected as Rhodes Scholar for South Australia in 1911, but this was evidently held over as Madigan was a member of Mawson's Australian Antarctic Expedition, 1911-14.

During World War I Madigan served with the Royal Engineers, gaining his captaincy in 1916. He took part in the Battles of Loos, Somme, and Arras, was twice wounded and was mentioned in despatches.

Proceeding to Oxford, Madigan graduated B.A. with First Class Honours in Natural Science (Geology) in 1919. He took his M.A. degree in 1922 and in 1933 was awarded the D.Sc. of Oxford for his research work in South Australia. After leaving Oxford he joined the Sudan Civil Service in 1920, but resigned on being appointed Lecturer in Mineralogy and Petrology at the University of Adelaide.

Madigan was an active worker in little-known parts of central Australia and led excursions on several occasions to this area. He made an aerial reconnaissance of portion of central Australia in 1929, paying particular attention to the Lake Eyre district. He explored and geologically mapped portions of the MacDonnell Ranges, the Jervois Ranges, etc., and in 1939 was the leader of the Simpson Desert Expedition.

He summarized his researches on central Australia in his presidential address to the Geography Section of A.N.Z.A.A.S. in 1937 at Auckland, but has published further information since that date.

During World War II Madigan was given leave of absence from the University and was Chief Instructor at the School of Military Engineering near Liverpool, New South Wales. He was made Lt.-Colonel in 1941 but in 1942 left the Army to return to his duties at the University of Adelaide.

Madigan received the King's Polar Medal in 1914 and the Murchison Grant of the Royal Geographical Society to aid him in his work of exploration.

Among his non-scientific activities was his interest in the Boy Scout Movement, and for some time he was Chief Commissioner of Scouts for South Australia and was the leader of the South Australian contingent to the Jamboree in Melbourne. Madigan died early in 1947 at the age of fifty-eight years.

In 1930 A. R. Alderman was appointed Evening Lecturer in Geology at Adelaide.

Arthur Richard Alderman was born at Glenelg, South Australia, in 1901. He was educated at St. Peter's College, Adelaide, and the Universities of Adelaide and Cambridge. He graduated B.Sc. Adelaide in 1924 and M.Sc. in 1928. At Cambridge, Alderman entered Clare College and was awarded the Ph.D. degree for research carried out at Cambridge. In 1937 Alderman was appointed Research Assistant, and while holding this position carried on his research activities in petrology and on meteorites. Shortly after the outbreak of World War II he was seconded to the Division of Industrial Chemistry of the C.S.I.R., which had established laboratories at Fishermen's Bend, Melbourne. He has now resigned his appointment at Adelaide and joined the permanent staff of the C.S.I.R. Alderman was admitted to the degree of D.Sc. Adelaide in 1943.

From 1939 A. W. Kleeman has been Lecturer in Geology, first as Evening Lecturer and later as full-time Lecturer. Kleeman graduated B.Sc. Adelaide in 1933 and M.Sc. in 1935. He was appointed to the Aerial, Geological and Geophysical Survey of North Australia in 1936.

In 1946 Aleck William Whittle, B.Sc., was Evening Lecturer and in 1947 Allan Frazer Wilson, M.Sc., was appointed a Temporary Lecturer and Donald Ralph Bowes, B.Sc., was appointed Demonstrator.

Hector Brock, who for many years has been Chief Technical Assistant, is now ranked as Demonstrator and Technical Assistant.

TASMANIA.

The Act to establish the Tasmanian University, as it is called in the Act, was assented to in 1889 and three lecturers were appointed in 1892. These lecturers were later made professors. In 1896 details of Geology I in the second year of the Science course and Geology II in the third year were published. In 1903 details for Geology Parts I, II and III appear—Geology I being taken in the first year of the Science course, but there does not appear to have been any formal instruction provided. In the Calendar for 1899 William Alexander MacLeod, B.A., B.Sc. (N.Z.), is named as Lecturer in Chemistry, but remained on the staff for a very short time because in 1901 Peter James MacLeod, B.A., B.Sc. (N.Z.), was appointed Lecturer in Chemistry, Assaying, etc., and W. A. MacLeod is not mentioned. Both the MacLeods took out the B.A. from the University of Otago (N.Z.) in 1895 and W. A. MacLeod took the B.Sc. in 1897,

so that the B.Sc. after P. J. MacLeod's name was an error and does not appear in subsequent Calendars. P. J. MacLeod remained Lecturer in Chemistry, Assaying, etc., until 1905, when his title was changed to that of Lecturer in Chemistry and Geology and Fritz Joseph Ernst, B.Sc., was appointed Assistant Lecturer in Geology. F. J. Ernst graduated in 1904 and had evidently passed examinations in Geology, possibly under the tuition of P. J. MacLeod.

In the 1906 Calendar the name of F. J. Ernst again appears as Assistant Lecturer, but was noted as being on leave. No further mention of Ernst appears, although P. J. MacLeod's title remained that of Lecturer in Chemistry and Geology until 1915, when his title was changed to Lecturer in Chemistry. No further change appeared until the Calendar for 1918-19, in which the details for Geology Parts I, II and III contain the following notes :

"After 1918 examinations in this subject will not be held until satisfactory arrangements can be made for the instruction of candidates."

Conditions remained unchanged until 1926, when the note quoted above was omitted. In the following year new enlarged details for Geology Parts I and II were published but there was no mention of Geology Part III. In 1928 details for Geology Part III were again included and three part-time Lecturers in Geology were appointed :

Arndell Neil Lewis, M.C., LL.M. (Tas.).

Alexander McIntosh Reid.

Percival Bartlett Nye, M.Sc., B.M.E. (Melb.).

In 1929 a note appeared above the details for Geology II and III as follows :
"At the time of going to press arrangements for lectures and laboratory work have not yet been completed. It is hoped that an announcement will be made at a later date."

In 1930 no details were given for Geology II and III, though those for Part I were published. A. N. Lewis was, in 1930 and 1931, the only Lecturer in Geology.

A. McIntosh Reid and P. B. Nye were only on the staff for about a year, and both are better known for their work on the Tasmanian and other surveys than for academic work, so that no details of their training, etc., are given here. On the other hand no person has done as much to advance the teaching of geology in Tasmania as A. N. Lewis.

Arndell Neil Lewis was born at Perth, Tasmania, in 1897. He was educated at Leslie House School (now Clemes' College) and the University of Tasmania. At the University he studied law and graduated LL.B. in 1922, LL.M. in 1925 and LL.D. in 1930. Early association with R. M. Johnson laid the foundation of his interest in geology and while studying law he found time to take a wide interest in geology, more especially in respect to glaciation in Tasmania.

After graduating in Tasmania he went to Melbourne to do some extra reading in law, and while there attended as many classes in geology at the University as he could fit in. Arrangements were made for him to attend lectures and laboratory work in any of the courses in which he was interested and he attended all field excursions that were held during his stay in Melbourne. This extra work no doubt widened his knowledge, but he will long stand as an example of what can be done in self instruction by a person with brains, perseverance and enthusiasm. On his return to Tasmania he continued to extend his knowledge, especially of the glacial and physiographic features of the island, and soon became the foremost authority on Tasmanian glaciation. He served in the first world war, holding a commission (lieutenant) with the First Field Artillery, and won the M.C. After the war he served in the A.M.F., rising to Captain in 1924, Major in 1928, and Lt.-Colonel in 1933. Among other activities it may be mentioned that he was Chairman of Trustees of the Tasmanian Museum

and member for Denison in the State Parliament. He died in December, 1943, at the early age of forty-six.

In the Calendar for 1932 no provision was made for the teaching of geology, but details for Geology Part I appear.

No change occurred during the next two years, but in 1935 geology is grouped with physics under Professor A. L. McAulay, but with a note that a Lecturer in Geology (part-time) was to be appointed. No one appears to have been appointed in that year or the next. In 1938 the Department was still Physics and Geology, but no mention was made of an appointment in geology and no details for geology were published. In that year P. J. MacLeod resigned and was replaced by Ernst Edgar Kurth, D.Sc., who later became Professor of Chemistry.

Geology was apparently entirely dropped from 1938 to 1945, but in 1946 S. W. Carey was appointed the first Professor of Geology in the University of Tasmania, and early this year Maxwell Robert Banks, B.Sc., was appointed Lecturer. It is to be hoped that from now on the teaching of geology will be on a much more satisfactory footing than in the past.

Samuel Warren Carey graduated in the University of Sydney B.Sc. in 1933, M.Sc. in 1934 and D.Sc. in 1939. He was on active service during the second world war and soon after his demobilization he became Chief Geologist on the Tasmanian Geological Survey and from that position transferred in 1946 to the newly established Chair of Geology in the University of Tasmania.

QUEENSLAND.

The University of Queensland was opened in 1910. One of the early appointments was that of H. C. Richards, who was elected Lecturer-in-Charge of Geology in 1911.

Henry Caselli Richards was born at Melton, Victoria, in 1884, and received his early training in Geology at the University of Melbourne, where he graduated B.Sc. in 1907, M.Sc. in 1909 and D.Sc. in 1915.

He was the second holder of the Caroline Kay Scholarship in Geology and subsequently held a Government Research Scholarship, but resigned this Scholarship to become Lecturer-in-Charge, Chemistry and Mining Department of the Technical School, Brisbane, and held this post during 1910-11, and then resigned to accept the Lectureship in Geology at the newly established University of Queensland.

In 1919 the Chair of Geology was founded and Richards became the first Professor of Geology in the University of Queensland. He was still the holder of the Professorship at the time of his death this year. He has left behind him a long record of research ably accomplished. Richards has filled many important posts, such as President of the Professorial Board, 1925-31; Deputy Chancellor of the University of Queensland, 1946; Chairman of the Great Barrier Reef Committee since 1925, when he was instrumental in its establishment. He was also Chairman of the Queensland Committee of the C.S.I.R. from 1926.

Richards was President of Section C (Geology), A.A.A.S., in 1924 at the Adelaide meeting. In his presidential address he summarized and brought up to date our knowledge of the volcanic rocks of Queensland. He was also a member of the Executive of the Australian National Research Council from 1923 to 1932.

Richards was associated with Markham on a survey of Museums and Art Galleries in Australia under the auspices of the Carnegie Corporation of New York. The report was published in 1933 and as a result of certain recommendations the Art Galleries and Museums Association of Australia and New Zealand was formed and Richards was President in 1937. Richards was in charge of the teaching of geology at the University since its establishment and,

aided by very able assistants, has set a standard, as to administration, teaching and research which it will be difficult to find equalled in any other University of similar age and size.

In 1913 A. B. Walkom was appointed Lecturer in Geology at the University of Queensland.

Arthur Bache Walkom was born at Grafton, New South Wales, in 1889 and was educated at Fort St. School and the University of Sydney, where he graduated B.Sc. in 1910 and D.Sc. in 1918. He was Macleay Fellow of the Linnean Society of New South Wales during 1912-13 and then joined the staff of the Geological Department of the University of Queensland, but resigned in 1919 to accept the Secretaryship of the Linnean Society of New South Wales. He was appointed Director of the Australian Museum in 1940, a position which he still holds.

While in Queensland Walkom was Honorary Secretary of the Royal Society, 1916-18, and President, 1918-19. He also carried out extensive research on the fossil flora of Queensland, particularly that belonging to the Mesozoic period, and published numerous papers in the Royal Society of Queensland and elsewhere. In 1929 Walkom attended the British Association meeting in South Africa, and in 1930 was given six months' leave, and while holding a Rockefeller Foundation Scholarship spent some time studying palæobotany under Seward. In 1933, at the invitation of the Geological Society of America, Walkom attended the Sixteenth International Geological Congress at Washington. He was Secretary of the Linnean Society from 1919 to 1940 and President 1941-42. He was President of the Royal Society of New South Wales 1943-44.

The A.N.Z.A.A.S., formerly the A.A.A.S., owes a debt of gratitude to Dr. Walkom for his long and able service as Honorary General Secretary from 1926 to 1947.

Dr. Walkom is the leading authority on fossil plants in Australia and has made the Mesozoic flora of Australia his special subject of research.

Walkom was succeeded as Lecturer in Geology by W. H. Bryan in 1920.

Walter Heyward Bryan was born at Brisbane in 1891. He was educated at Ipswich Grammar School and the Universities of Queensland and Cambridge. He graduated B.Sc. in 1914, M.Sc. in 1916 and D.Sc. in 1926. He joined the Geological Survey of Queensland in 1914 but resigned in 1915 to enlist in the A.I.F. for active service in World War I. He served in Gallipoli and France and was mentioned in despatches and awarded the M.C.

Soon after being demobilized, Bryan was appointed Lecturer in Geology at the University of Queensland. In 1946 the Council of the University of Queensland conferred the well-merited title of Associate Professor of Geology on Dr. Bryan.

Bryan was President of the Royal Society of Queensland in 1924. His research work has dealt with many branches of geology, perhaps more especially with palæogeography, and his publications are numerous and of a uniformly high standard.

In 1926 the Geological Department had grown to such an extent that another senior member of staff became necessary, and F. W. Whitehouse was appointed Lecturer.

Frederick William Whitehouse was born at Ipswich in 1900 and was educated at the Ipswich Grammar School and the Universities of Queensland and Cambridge. He graduated B.Sc. in 1922 with First Class Honours and University Gold Medal. Whitehouse was awarded a Queensland University Foundation Travelling Scholarship, and this allowed him to enter Cambridge, where he won the Ph.D. degree. In 1926 he was appointed to the John Thomson Lecture-ship in Geology at the University of Queensland. Prior to the war he did extensive field work in north-western Queensland and central Australia. In

1941 he enlisted in the A.I.F. and served in New Guinea and northern Australia. He gained his commission in 1942. Whitehouse won the D.Sc. Queensland in 1939. He has been Honorary Palaeontologist to the Queensland Museum and Palaeontologist to the Geological Survey of Queensland. The main interest of Whitehouse has been in palaeontology, and he has published many valuable papers on this subject, more particularly in respect to Cambrian and Cretaceous faunas, and has, in addition, published many other papers on general and structural geology.

In 1940 A. O. Jones was appointed Lecturer in Geology. Arthur Owen Jones graduated B.Sc. in the University of Queensland in 1925 and M.Sc. in 1927.

In 1946 Dorothy Hill was also appointed a Lecturer. Dorothy Hill graduated B.Sc. in 1928, M.Sc. in 1930, and D.Sc. in 1942. In addition Dr. Hill studied at Cambridge and won the Ph.D. of that University. During the second world war Dorothy Hill held a commission in the W.R.A.N.S. She is now one of our leading palaeontologists and has specialized in the Corals and Bryozoa, and has published numerous papers, principally in the *Proceedings of the Royal Society of Queensland*.

Two other recent appointees are Edward Valentine Robertson, B.A., who was Demonstrator from 1941 to 1945, and was then appointed Temporary Lecturer, and Jack Tunstal Woods, who graduated B.Sc. in 1946 and has been Demonstrator in Geology in 1946-1947.

WESTERN AUSTRALIA.

The University of Western Australia was opened in 1912 and Geology was among the Foundation Chairs. The first Professor was Walter George Woolnough.

Woolnough was born in 1876 at Brushgrove, New South Wales, and was educated at Newington College and the University of Sydney, where he graduated B.Sc. in 1898 and D.Sc. in 1904, being the first person to be admitted to this degree at the University of Sydney.

After graduating, Woolnough was appointed Demonstrator in Geology in Sydney, but resigned in 1902 to become Lecturer in Geology and Mineralogy at the University of Adelaide. This post was established after the death of Professor Tate, when the work in geology was divided between W. Howchin and W. G. Woolnough, both with the title of Lecturer. Woolnough resigned from Adelaide in 1905 and returned to Sydney as Lecturer in Geology under Professor David. He was Acting Professor of Geology during David's absence with the Shackleton Antarctic Expedition, 1907-09. In 1911 Woolnough was made Assistant Professor of Geology in the University of Sydney, but transferred in the following year to Western Australia to become the first Professor of Geology in the newly established University of Western Australia. During World War I Woolnough began investigating salt deposits in Australia on behalf of the Brunner Mond Co. (now Imperial Chemical Industries). This work was of national importance and finally as the work necessitated so much travelling, etc., he felt obliged to resign his Chair. Woolnough remained with Brunner Mond until 1927, when he became Geological Adviser to the Commonwealth Government from 1927 till his retirement in 1941. During World War II his services were retained and he became Chief of Information Section, Directorate of Technical Practice, Ministry of Munitions, Melbourne.

In 1897 Woolnough was a member of David's party at Funafuti and he was the leader of expeditions to Fiji in 1901 and 1905. In all these undertakings valuable geological and geographical information was obtained. In 1911 the Commonwealth Government sent a scientific expedition to the Northern Territory and Woolnough was the chief geologist of the party. He was the Chairman of

the Royal Commission on the Collie Coal Industry, Western Australia, in 1914-15. During his time with Brunner Mond, Woolnough travelled over much of central Australia, especial attention being paid to salt lakes such as Lake Eyre.

As Geological Adviser to the Commonwealth, he had to report on oil, and was sent by the Government to study the oil areas of the United States. This was in 1930, and two years later Woolnough carried out the first aerial survey of the possibilities of oil in Australia.

At the Auckland meeting of the A.N.Z.A.A.S. in 1937 Woolnough was President of Section C (Geology), where he gave an address on Fact and Theories in Geology, with Special Reference to Petroleum, Salt and Coal. He was President of the Royal Society of New South Wales, 1926-27.

During the absence of Woolnough with Brunner Mond, Marcel Auroousseau, a graduate of Science of the University of Sydney, was appointed Lecturer-in-Charge and carried on after Woolnough's retirement until he left to join the Carnegie Geophysical Institute of Washington in 1920. During the latter portion of 1920, after Auroousseau's departure, Howard Bolitho Hauser, B.Sc., Melbourne, took over the work of the Department until the end of the year. The Council of the University decided not to make another appointment of a Professor, and in 1921 Edward de Courcy Clarke was appointed Lecturer-in-Charge of Geology.

Clarke was born in New Zealand in 1880, and was educated at the High School, Napier, New Zealand, and at University College, Auckland, where he graduated B.A. in 1901 and M.A. in 1902. After holding the position of Science Master at the Auckland Grammar School from 1901-05, Clarke joined the Geological Survey of New Zealand, but in 1910 returned to University College, Auckland, as Demonstrator in Geology, but soon left to join the Geological Survey of Western Australia. In 1921 he resigned from the Survey to become Lecturer in Geology at the University. The position was raised to the status of Associate Professor in 1926 and to Professor in 1930. Professor de Courcy Clarke has had charge of the Geological Department of the University of Western Australia for over twenty-six years, and although for a large portion of that time he had little if any assistance in running his Department, he has managed to do much research work and to publish many important papers dealing with the geology of Western Australia.

Clarke was President of Section C (Geology) of the A.N.Z.A.A.S. in 1930 at Brisbane, and gave an important address on the Pre-Cambrian rocks of Western Australia.

In 1934 Rex T. Prider was appointed Assistant Lecturer, and Lecturer in 1939.

Rex Prider graduated B.Sc. in 1932, and later at Cambridge won the Ph.D. in 1938. He was admitted to the degree of D.Sc. (Western Australia) in 1946.

At present R. W. Fairbridge is also Lecturer in Geology. He graduated B.Sc. at Oxford, B.A. Canada and D.Sc. Western Australia in 1944.

Dorothy Carroll, who graduated B.Sc. in 1922 and later Ph.D. London in 1936, has done excellent work on microscopic examination of soil particles and held a Research Fellowship from 1939.

Curt Teichert (see above under "Melbourne") also held a Research Fellowship for a period.

This brings the history of the Teachers of Geology in Australian Universities up to 1947, and covers a period of nearly one hundred years in the case of Melbourne with lesser periods in the case of other Universities.

While most of those who were appointed in the early days of geological education in Australia were from overseas, most of the later appointments to Professorships or Lectureships have been from Australian-

trained if not Australian-born graduates. Queensland is unique in that every person who holds or has held a senior post on the staff of the Geological Department of the University was born in Australia—Richards (Victoria), Walkom (New South Wales), Bryan, Whitehouse, Jones and Dorothy Hill (Queensland), and at the present time all members of staff are Queenslanders. It may be noted that at present Sydney has only Sydney graduates on the staff of its Geology School, and likewise Melbourne has only Melbourne graduates on its staff, except in the case of Dr. Teichert. There are two members of the teaching staff of the Department of Geology in Tasmania, and both are graduates of the same University—that of Sydney.

This concentration of graduates from a single University is probably not the wisest arrangement and would be truly dangerous but for the fact that young graduates are encouraged to go abroad to study at older Universities either with or without the idea of obtaining the Ph.D. degree. In this way their ideas and methods of teaching, research, etc., are widened and contacts with fellow workers in overseas Universities are established. Even then there has been the tendency for Sydney graduates to concentrate rather on Cambridge and Melbourne on the University of London.

To my mind it is certain that a round-table conference between the Professors of Geology in Australia to discuss questions of overseas study and future staffing would lead to a better and wider distribution of knowledge than occurs under the present system, and I would recommend the idea of such a conference to their serious consideration.

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PART III

THE COLORIMETRIC DETERMINATION OF IRON IN CANNED FOODS WITH 1, 10 PHENANTHROLINE.

By HUGH A. MCKENZIE, M.Sc.

Manuscript received, July 10, 1947. Read, August 6, 1947.

INTRODUCTION.

Investigations in this laboratory on the corrosion of tinsplate containers by foodstuffs frequently require trace iron determinations. While there is no lack of information in the literature on chromogenic agents for iron, comparatively few are well suited to the quantitative determination of small amounts of iron. (Sandell, 1944.)

The characteristics of the more common reagents have been examined by Woods and Mellon (1941), who concluded that the most generally suitable were 1, 10 phenanthroline (ortho-phenanthroline) and 2, 2' dipyridyl. Phenanthroline is colourless and reacts stoichiometrically with ferrous iron to form the intensely orange red coloured tris 1, 10 phenanthroline ferrous ion which is stable for long periods over the pH range 2 to 9. The complex ion obeys Beer's Law over a wide range of concentration. Phenanthroline is somewhat superior to dipyridyl as its complex is stable over a wider pH range and it is more readily available at a cheaper price. It will be seen later that it has the further advantage in the present application of being less subject to interference by citrate.

In the above corrosion experiments it is frequently necessary to determine iron in the presence of many times its amount of tin. Evidence was soon obtained which indicated that tin could interfere in the iron determination. It was therefore necessary to pay special attention to this interference.

A colorimetric method has been developed which involves wet digestion, use of p-hydroxy phenyl amino acetic acid (glycin) as reductant and 1, 10 phenanthroline as chromogenic agent.

BASIS OF THE METHOD.

Destruction of Organic Matter.

For reasons which have been adequately discussed by Piper (1942) wet digestion was chosen in preference to dry ashing for destruction of organic matter.

The Reduction.

The colour reaction with phenanthroline is given by ferrous but not by ferric iron. Since the iron is present as ferric sulphate after digestion it is necessary to reduce it to the ferrous state. A review of the literature indicates a rather confusing, and in some cases contradictory, mass of information on the use of reductants for trace iron determinations.

Saywell and Cunningham (1938) studied several reducing agents, including hydroxylamine hydrochloride, sodium hypophosphite and sodium formate; but finally used hydroxylamine on account of its freedom from iron. Hummel and Willard (1938) found sodium dithionite (hydrosulphite) unsatisfactory and employed hydroquinone with success. Fortune and Mellon (1938) found sodium sulphite, sodium formate and formaldehyde unsatisfactory and used

hydroxylamine hydrochloride. Dauphinee and Campbell (1937) found *p*-hydroxy phenyl amino acetic acid (the photographic, chemical glycine) to be suitable.

It will be seen later that it is necessary to carry out the colour reaction in the presence of sodium citrate. Cowling and Benne (1942) found that hydroxylamine hydrochloride was unsatisfactory under such conditions and used hydroquinone. The present author has found that in his procedure glycine is entirely satisfactory and superior to hydroquinone. Using glycine as reductant, maximum colour development for the maximum amount of iron determined took five minutes at 25° C., whereas at least 30 minutes were required with ten times as much hydroquinone.

Gerber *et al.* (1942) claim that glycine solution must be made up fresh each day. The present author has found that glycine solution (0.1 per cent. in 0.4 N sulphuric acid) stored for one month at 25° C. is still effective as reductant. It is of interest to note that both hydroquinone and glycine solutions must be prepared in acid solution for maximum stability.

The Colour Reaction: The Interference of Diverse Ions.

A critical examination of the influence of some fifty ions on the determination of iron with phenanthroline was made by Fortune and Mellon (1938). It was found difficult to make a general statement regarding the interference of an ion since the extent of interference frequently depended on the procedure followed.

Some attempt has been made to examine the effect of interfering ions on the determination in biological materials, but this work has been restricted to methods involving dry ashing.

The influence of certain elements which could possibly interfere in the determination and be present in canned foods in appreciable amounts was, therefore, examined.

(i) *Tin*. Known amounts of iron were determined in the presence of definite amounts of tin in synthetic solutions which had been subjected to the usual digestion. The method of determination was similar to that described in the recommended procedure, except that no sodium citrate was present. (Ammonium acetate was used as buffering agent.) There was no significant error in the determination of 25 microgrammes (γ) (5 p.p.m.)* of iron in the presence of 500 γ (100 p.p.m.) of tin but for 1,250 γ (250 p.p.m.) and 2,500 γ (500 p.p.m.) of tin the error was about -10 per cent. Even if the solutions were allowed to stand overnight there was no change in the interference.

The amounts of glycine and phenanthroline used were equivalent to 350 and 750 γ of iron respectively. With smaller amounts of glycine and phenanthroline the error was usually greater and could be as high as -20 per cent. Interference was sometimes observed in the presence of only 500 γ of tin, when half the amount of glycine and one-quarter the amount of phenanthroline were used. While excess of reductant and chromogenic agent did have some effect on the interference, it was not possible to eliminate it completely by this means.

It is well known that sodium citrate forms a very stable complex with both stannous and stannic tin. It was therefore decided to determine the effect of sodium citrate on the interference of tin in the iron determination. Citrates have actually been used by other workers in the determination of iron in biological materials (by phenanthroline). Cowling and Benne (1942) used small amounts of ammonium citrate to overcome the interference of aluminium phosphate in the determination. Bandemer and Schaible (1944) used sodium citrate for adjustment of the pH, in preference to acetate. They observed that the rate of colour formation was retarded by citrate.

* The figures in brackets are the original metal contents expressed as p.p.m. assuming the metal came from 5 g. of food.

Determinations carried out by the author on pure iron solutions using sodium citrate as buffering agent confirmed this effect. At 25° C. colour formation took at least 30 minutes to develop completely whereas at 12° C. several hours were required. Colour development at both temperatures using ammonium acetate was almost instantaneous.

A modified procedure was, therefore, tried involving a smaller amount of sodium citrate (1 ml. of N in 50 ml. solution) and using N ammonium acetate as buffering agent. In digests of pure iron solutions the colour for 25 γ of iron was completely developed within four minutes at both 25° C. and 12° C. The colour for 200 γ was developed within five minutes at 25° C. and 10 minutes at 12° C.

The determination of iron in the presence of tin was then repeated using the smaller amount of sodium citrate. The results are shown in Table 1. It is seen that there is no significant error introduced by the presence of as much as 2,500 γ of tin. The readings were taken after fifteen minutes, which is sufficient for maximum colour development.

It is of interest that the retardation effect of citrate was present when determinations were made on solutions of ferrous iron. At the pH of the reaction sodium citrate probably forms a strong complex with the iron (Lingane, 1946) from which the phenanthroline has some difficulty in removing the iron.

Sodium citrate exerts a greater retarding influence on the development of the colour with 2,2' dipyridyl, making this reagent less suitable when the colour reaction is carried out in the presence of citrate. This greater effect for dipyridyl may be associated with the somewhat greater instability constant of its iron complex (Dwyer and Nyholm, 1946; Dwyer and McKenzie, 1947).

(ii) *Zinc*. Morgan and Rawlings (1943) have shown that it is unlikely that the zinc content of foods would exceed 100 p.p.m. Zinc can form a colourless complex with phenanthroline, but it is doubtful if it would interfere in these amounts with the large excess of phenanthroline which is used in the recommended procedure. This has been tested experimentally and the results in Table 1 show that the only appreciable interference is in the determination of 200 γ (40 p.p.m.) of iron in the presence of 2,500 γ (500 p.p.m.) of zinc. So that there is no interference by zinc in the amounts which might reasonably be present in canned foods.

(iii) *Copper*. According to Morgan and Rawlings (1943) the copper content of foods rarely exceeds 50 p.p.m., this figure probably only being reached by tomato products. Copper may form a weakly coloured complex with phenanthroline, and its extent of interference was therefore studied. The results in Table II show that even as much as 250 γ (50 p.p.m.) of copper produce no appreciable interference.

(iv) *Nickel*. It is doubtful if the nickel content of canned foods would exceed 5 p.p.m. Nickel forms a weakly coloured complex with phenanthroline. The results in Table I show that amounts of nickel up to 250 γ (50 p.p.m.) produce no significant interference.

(v) *Calcium*. Certain canned foods may have very high natural calcium contents, e.g. silver beet 6,000 p.p.m., whereas others may have high contents due to treatment with calcium chloride brines during processing, e.g. potatoes 2,000 p.p.m. The diluted digests of such foods always show appreciable precipitates of calcium sulphate. The possible interference by adsorption was therefore examined. The results in Table I show no appreciable interference.

(vi) *Phosphorus*. Pyrophosphate interferes badly in the determination of iron in methods involving dry ashing unless the ash solution is specially treated, but in wet digestion pyrophosphate is transformed to orthophosphate from which there is probably little interference. The results shown in Table I verify this.

TABLE I.
Influence of Diverse Elements on the Determination.

Micrograms of Iron per 50 ml.	Original Iron Content. p.p.m.	Added Element.	Micrograms of Added Element.	Original Content of Added Element. p.p.m.	Iron Content Found. p.p.m.	Error per Cent.
25	5	Tin	500	100	4.8	-4
25	5	"	500	100	4.9	-2
25	5	"	500	100	5.0	0
25	5	"	500	100	5.0	0
25	5	"	1,250	250	4.9	-2
25	5	"	1,250	250	5.1	+2
25	5	"	1,250	250	5.0	0
25	5	"	1,250	250	5.0	0
25	5	"	2,500	500	5.1	+2
25	5	"	2,500	500	5.0	0
25	5	"	2,500	500	5.1	+2
25	5	"	2,500	500	5.2	+4
25	5	Zinc	500	100	5.0	0
200	40	"	500	100	40.0	0
25	5	"	1,000	200	4.9	-2
200	40	"	1,000	200	40.0	0
25	5	"	2,000	400	4.9	-2
200	40	"	2,000	400	39.5	-1
25	5	"	2,500	500	5.0	0
200	40	"	2,500	500	36.8	-8
25	5	Copper	100	20	5.0	0
25	5	"	100	20	4.9	-2
25	5	"	250	50	5.0	0
25	5	"	250	50	4.9	-2
25	5	Nickel	100	20	5.0	0
25	5	"	100	20	5.0	0
25	5	"	250	50	4.9	-2
25	5	"	250	50	4.9	-2
10	2	Calcium	25,000	5,000	2.0	0
25	5	"	25,000	5,000	5.0	0
50	10	"	25,000	5,000	9.9	-1
25	5	"	50,000	10,000	4.9	-2
25	5	"	50,000	10,000	4.9	-2
25	5	Phosphorus	20,000	4,000	4.9	-2
25	5	"	20,000	4,000	5.0	0
25	5	Aluminium	500	100	4.9	-2
		phosphorus	2,500	500		
		Aluminium	2,500	500	5.1	+2
		phosphorus	2,500	500		
25	5	Aluminium	2,500	500	4.9	-2
		phosphorus	2,500	500		

Note.—The amounts of iron and added element are expressed as micrograms present in 50 mls. of solution. They are also expressed as p.p.m. assuming this amount of element came from 5 g. of food.

(vii) *Aluminium.* Cowling and Benne (1942) found that aluminium and phosphate interfered in the determination of iron, if the ratio of aluminium to iron were greater than two to one, by co-precipitation of iron with aluminium phosphate, unless citrate was present. The extent of aluminium phosphate interference was examined in the present work and as can be seen from Table I is negligible. With the higher amount of aluminium (500 p.p.m.) and phosphorus (500 p.p.m.) a precipitate occasionally occurred at the end of the digestion

TABLE II.
Recovery Tests in Canned Foods.

Food.	Iron Content.				$100\frac{b}{a}$
	Initial p.p.m.	Added p.p.m.	Calculated (a) p.p.m.	Found (b) p.p.m.	
Orange juice	3.0	2.0	5.0	5.0	100
	5.1	10.0	15.1	14.8	98
	2.3	5.0	7.3	7.2	99
	3.5	20.0	23.5	23.4	100
Potatoes	5.8	2.0	7.8	8.6	110
	5.8	5.0	10.8	10.8	100
	5.0	5.0	10.0	9.8	98
	5.0	20.0	25.0	25.1	100
Beetroot	3.4	5.0	8.4	8.4	100
	7.2	10.0	17.2	17.5	102
Silver beet	16.4	10.0	26.4	26.8	102
	17.7	10.0	27.7	28.0	101
	15.4	5.0	20.4	20.1	98
Cabbage.. ..	23.5	5.0	28.5	28.9	101
	14.9	10.0	24.9	25.1	101
Peaches	3.0	10.0	13.0	12.9	99
Asparagus	4.1	10.0	14.1	14.3	102
Tomatoes	10.0	10.0	20.0	20.6	103
	10.0	20.0	30.0	30.3	101
	12.4	10.0	22.4	23.1	103
Beans	9.2	10.0	19.2	19.2	100

which subsequently interfered, but if the diluted digest were boiled this precipitate dissolved. It is extremely unlikely, however, that the aluminium content would exceed 100 p.p.m.

Measurement of the Colour.

The absorption curve for the tris 1, 10 phenanthroline ferrous ion shows a maximum at 508 m μ with a secondary maximum at 474 m μ . On the Evelyn photoelectric colorimeter maximum absorption is given by the 490 and 470 m μ filters. Beer's Law is obeyed for the 490 filter only over the range 10 to 100 γ (per 50 mls.) of iron, but for the 470 filter over the whole working range 10 to 200 γ of iron, and the latter has, therefore, been used for the colour measurement.

RECOMMENDED PROCEDURE.

Reagents.

Water: Distilled water, redistilled from Pyrex.

Nitric Acid: 16 N. A.R. (Redistilled if necessary.)

Sulphuric acid: 36 N. A.R. (Redistilled if necessary.)

Hydrogen peroxide: 30 per cent. (100 volume). B.P.

Sodium citrate: 25 g. dissolved in 100 mls. of water.

P-hydroxy phenyl amino acetic acid.

Photographic glycine: 0.1 g. dissolved in 100 mls. of 0.4 N sulphuric acid.

1, 10 phenanthroline: 0.4 gm. dissolved in 100 mls. of 2 per cent. acetic acid.

Ammonium hydroxide: Concentrated A.R. redistilled from Pyrex.

Ammonium acetate: A.R. 70 g. dissolved in 1 litre of water.

Apparatus.

A spectrophotometer or photoelectric colorimeter.

(An Evelyn photoelectric colorimeter manufactured by the Rubicon Co., Philadelphia, U.S.A., was used by the author.)

The water was redistilled in the apparatus described by Piper and Oertel (1941).

Method.

Mix the sample of food with nitric acid (20 mls.) and sulphuric acid (10 mls.) in a Kjeldahl flask (500 mls.).

(Note.—50 g. samples are usually taken, representative sampling being obtained by homogenization in the Waring Blender. This sample size is used because determinations of several metals are made on the final digest.)

The digestion procedure, involving the use of hydrogen peroxide, has been described in detail by McKenzie (1945). Make up the digest to 50 mls. Transfer a 5 ml. aliquot, preferably containing 20 to 200 γ of iron, to a 50 ml. volumetric flask. To this add sodium citrate solution (1 ml.), glycine solution (1 ml.) and phenanthroline (2 ml.).

From a burette add the amount of ammonium hydroxide required to give a pH of approximately 3.8. Make up to volume (50 mls.) with ammonium acetate. Remove any precipitate by centrifuging. Allow to stand for 15 minutes after making up to volume. Read the transmittance on the photoelectric colorimeter (470 m μ filter for the Evelyn colorimeter) or spectrophotometer.

Recovery Tests.

Satisfactory evidence for the validity of the method is given by the recovery tests in pure solutions described above. Recovery tests in canned foods provide useful confirmatory evidence, although this is somewhat circumstantial particularly when the initial iron content is high.

Typical recovery tests are shown in Table II. The precision and reproducibility of the method are seen to be of the order of ± 3 per cent.

The following advantages are claimed for the method: (a) The method of wet digestion is very simple and safe; (b) there is no significant interference from insoluble matter; (c) the procedure is highly specific and not subject to interference from elements which might be present in canned foods, tedious separations being thereby eliminated; (d) the pH need not be accurately controlled; (e) the time for a determination is short.

SUMMARY.

A rapid, highly specific, method is described for the determination of iron in canned foods, using a wet digestion procedure, and a colorimetric determination with 1,10 phenanthroline as chromogenic agent and p-hydroxy phenyl amino acetic acid (glycine) as reductant. It is shown that sodium citrate must be present to overcome interference by tin, and that in the presence of citrate glycine is the most satisfactory reductant. Dipyriddy is unsuitable as chromogenic agent when citrate is present.

Recovery tests on pure solutions in the presence of various added elements and on canned foods show that the precision and reproducibility of the method are of the order of ± 3 per cent.

ACKNOWLEDGMENTS.

The author is indebted to Miss H. Smith for her assistance during this investigation and also to Mr. E. Thompson and Miss A. White for synthesis of samples of phenanthroline.

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THE REACTION OF PYRIDINE WITH DICHLOROTETRAMMINE COBALT (III) COMPLEXES.

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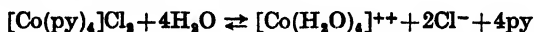
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In the course of an investigation of the polarographic behaviour of ammonia and ethylenediamine complexes of cobalt (III) (Willis, Friend and Mellor, 1945) an attempt was made to prepare the penta- and hexa-pyridine salts of the metal by heating trans-dichloro-tetrapyridine cobalt (III) chloride with excess of pyridine. Although the attempt was unsuccessful, it was thought that the reaction which did occur was of some interest since it involved the reduction of cobalt III to cobalt II. This reduction was unexpected because covalent octahedral complexes of cobalt III are usually stable as compared with those of cobalt II. For comparison, the reaction of pyridine with a number of other dichlorotetrammine cobalt III salts was also studied.

EXPERIMENTAL.

Reaction of Pyridine with Trans-dichlorotetrapyridine Cobalt (III) Chloride.

A small quantity (3.0 g.) of trans $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$, prepared by the method of Werner and Fenster (1906), was dissolved in 40 ml. of redistilled pyridine to give a green solution. This was evaporated on a water-bath until much of the pyridine had been driven off. During this process chlorine was evolved and could be detected by means of starch-potassium iodide. On cooling the solution, rose-pink crystals separated. Recrystallized from pyridine, in which they dissolved to give a blue solution, the pink crystals separated once more. The compound could be kept indefinitely in a stoppered tube but in the air it slowly turned blue. Analysis of the compound gave the following figures: Co, 13.4%; Cl, 15.4%. This suggested that the substance was $[\text{Co}(\text{py})_4]\text{Cl}_2$ (Co, 13.2%; Cl, 15.9%), a conclusion supported by molecular conductivity measurements on aqueous solutions. The value of μ_∞ , $250\omega^{-1}$, indicated dissociation into three ions, most likely as follows:



Evidence for the existence of this type of reaction is to be found in an earlier paper (Willis *et al.*, 1945).

That reduction had occurred during the reaction between trans-dichlorotetrapyridine cobalt (III) chloride and pyridine was confirmed by means of polarographic and magnetic measurements.

On polarographic examination, the compound $([\text{CoPy}_4])\text{Cl}_2$ was found to give a single step in 0.05 M K_2SO_4 with $E_1^1 = -1.185$ volts corresponding to a reduction from Co^{II} to Co^0 (Willis *et al.*, 1945).

The magnetic susceptibility of the compound was found to be $+21.2 \times 10^{-6}$ c.g.s. units. If it is assumed that its formula is $[\text{Co}(\text{Py})_4]\text{Cl}_2$, this gives a value of 9450×10^{-6} c.g.s. units for ψ_M at 21°C .; correcting for diamagnetism gives a value of 4.85 Bohr magnetons for μ , a value well within the range found for ionic cobalt II complexes or complexes with sp^3 bonds (Mellor and Goldacre, 1940).

The Reaction of Pyridine with Dichloro-bis-ethylenediamine Cobalt (III) Chloride.

On refluxing trans (green) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ with pyridine it did not dissolve but at first slowly turned dark purple (owing to conversion to the cis compound) and finally red. The cis compound

itself, when refluxed with pyridine, also turned red without dissolving. The red compound was identified, by its cobalt content, as $[\text{Co}(\text{en})_2\text{pyCl}]\text{Cl}_2$ (Co required by this formula, 15.0%; found, 15.6%).

The conversion was practically quantitative. There was evidence that traces of $[\text{Co}(\text{Py})_4]\text{Cl}_2$ were formed but undoubtedly the main reaction was the formation of the pentammine salt.

The Reaction of Pyridine with Dichlorotetrammine Cobalt (III) Chloride.

When trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is heated with pyridine it dissolves very slowly to give a green solution. At the end of two hours most of the original solid remained; on filtering and evaporating the filtrate $[\text{Co}(\text{py})_4]\text{Cl}_2$ separated out, indicating that partial reduction had occurred. On the other hand no reduction occurs if trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is treated with concentrated ammonia solution. Instead, the chloropentammine salt is readily formed (Werner, 1911).

DISCUSSION.

Although there is no doubt that the product of the interaction between $[\text{CoPy}_4\text{Cl}_2]\text{Cl}$ and pyridine is a cobaltous compound, it does not necessarily follow that pyridine acts directly as a reducing agent¹ in the ordinary sense of that term. The following mechanism may account for the reaction. The first step consists of the formation of an unstable complex, $[\text{CoPy}_5\text{Cl}]^{++}$ or $[\text{CoPy}_6]^{+++}$, whose oxidation-reduction potential is greater than 1.35 volts, the value of the oxidation-reduction potential of chlorine. The unstable complex then oxidizes chloride ion to chlorine and *is itself reduced to the cobalt II stage*. Among hexammine cobaltic ions,² ability to oxidize chlorine ion appears to be confined to the unstable $[\text{Co}(\text{py})_6]^{+++}$ and $[\text{Co}(\text{py})_2(\text{NH}_3)_4]^{+++}$. It is not shown by $[\text{Co}(\text{en})_3]^{+++}$, $[\text{Co}(\text{en})_2\text{pyCl}]$ or $[\text{Co}(\text{NH}_3)_6]^{++}$.

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¹ It is of interest to note the difference in behaviour of Co^{III} and Rh^{III} . The pentapyridine and hexapyridine complexes of Rh^{III} can be readily prepared. Private communication from Dr. F. P. J. Dwyer.

² Another instance of the apparent reducing action of pyridine is to be found in the chemistry of ruthenium. If $\text{K}_2[\text{RuCl}_5\text{H}_2\text{O}]$ is treated with excess pyridine, orange needles of the composition $[\text{Ru}(\text{Py})_4\text{Cl}_2]$ separate. The change in valency of the ruthenium can be followed by means of magnetic susceptibility measurements. The moment of Ru^{III} in the first compound is 2.05 Bohr magnetons; that of the Ru^{II} in the second is zero. (Unpublished experiments with Miss A. H. Cameron.)

A NEW METHOD FOR THE COMPARISON OF THE THERMAL CONDUCTIVITIES OF FLUIDS.

PART I.

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INTRODUCTION.

On account of the ease with which temperature differences in a fluid set up a system of convection currents the measurement of the thermal conductivity of a fluid has always been a singularly difficult problem in experimental physics, and, in consequence, reliable data for this property is relatively scarce. This is unfortunate in that the formulæ which have been developed for the treatment of the heat losses from various bodies in air, water or other fluids all involve the thermal conductivity of the fluid concerned. The magnitude of the thermal conductivity enters into such dimensionless parameters as the Peclet, Grashof, Prandtl and Nusselt numbers—all important in the treatment of thermal convection by the method of dimensions—and other more complicated quantities of a like nature, such as those concerned with the condensation of vapours. All this means that for many regular shaped bodies immersed in a given fluid we may calculate the convective heat loss to be expected if we know the thermal conductivity of the fluid concerned. It would seem reasonable therefore to attempt to reverse this process and calculate the thermal conductivity from measurement of the convective heat loss from bodies of known regular form immersed in the fluid.

Data on the heat loss from horizontal cylinders immersed in fluids are particularly well known and have been correlated by a relation between the Nusselt and the product of the Grashof and Prandtl numbers, viz. :

$$\frac{qd}{k\theta} = f\left(\frac{d^3 \rho^2 c g \beta \theta}{\eta k}\right) = f(ad^3\theta) \dots\dots\dots (1)$$

where

q is the heat flow per unit area per unit time from the heated surface.

d is the diameter of the heated cylinder.

k is the thermal conductivity of the fluid.

ρ is the density of the fluid.

β is the coefficient of thermal expansion of the fluid.

c is the specific heat (at constant pressure) of the fluid.

η is the viscosity of the fluid.

θ is the temperature difference between heated surface and bulk fluid.

g is the local value of the gravitational field

and $f(x)$ is an empirical function.

The composite property a is known as the convective modulus of the fluid. This property is related to other properties by

$$a = \frac{\rho^2 c g \beta}{\eta k} \dots\dots\dots (2)$$

From an analysis of data collected by McAdams (1941) the author (Bosworth, 1944) showed that the function $f(x)$ could, within the accuracy of the experimental data, be put in the form

$$f(x) = 0.40 + 0.44x^{1/6} + 0.12x^{1/3} \dots\dots\dots (3)$$

and suggested that the thermal conductivity of a liquid could be obtained from measured data on convective heat loss by plotting $f^{\frac{1}{6}}$ against $x^{1/6}$. The paper further suggested that a resistance wire with a fine thermocouple welded to the central portion could be used as the heated cylinder. The power consumed is proportional to the square of the heating current (I) and the temperature difference (θ) to the reading of the thermocouple. Accordingly equation (3) suggests that $I/\theta^{\frac{1}{6}}$ should be plotted against $\theta^{1/6}$, and the intercept of the resultant line taken as proportional to the root of the thermal conductivity while the slope is proportional to the sixth root of the convection modulus of the liquid concerned. By this means it was suggested that the thermal conductivities and convective moduli of all fluids not being electrical conductors could be determined in terms of the properties of some standard fluid.

The mode of operation as suggested in the earlier paper has one serious practical objection. In order that the extrapolation to zero θ should be reasonably accurate the range of values of θ for which measurements are obtained should be very extensive, a range of 4° or 4,000 to 1 being desirable. There is an upper limit to the useful range of θ set by the boiling point of the liquid. For many liquids the upper limit may be taken as about 40°C ., with still lower values for the more volatile liquids and possibly higher values for liquids of high boiling points. In order to get the desired range it would then be necessary that the lower value of θ should be 0.01°C . While a copper-constantan thermocouple and a laboratory galvanometer will detect a temperature difference of this order it is doubtful whether measurements of I^2/θ of the required accuracy could be obtained at such low values of θ , especially in view of the fact that a heated wire in a fluid shows transient phenomena (Bosworth, 1946) which appear to be of the longer time scale the lower the temperature difference. Accordingly it is considered that 0.1°C . is about the lowest value of θ for which measurements of I^2/θ at the required accuracy can be obtained. The requisite range of θ for the $1/6$ th power plot is therefore only attainable with the liquids of highest boiling point, and some other form of plotting is desirable in experimental work. For example it may readily be seen that equation (3), which after all is empirical and therefore approximate only, would give a straight line if $f(x)$ were plotted against $x^{1/3}$ provided x is not too small. Over a limited range of x we may always expand $f(x)$ in a Taylor series in powers of x or of \sqrt{x} . Let us write equation (3) in a more general form

$$\frac{qd}{k\theta} = \text{Const.} + f(ad^3\theta) \dots\dots\dots (4)$$

which postulates a physical condition in which the heat flow (per unit area per unit time) could be divided into two parts: one directly proportional to the temperature difference and to the thermal conductivity and the other proportional to a power of the temperature difference greater than the first and involving also the convective modulus as well as the thermal conductivity of the fluid.

THE EFFECT OF VARYING THE ORIENTATION OF THE HEATED SURFACE.

Any attempt to generalize equation (4) beyond the condition of applying to horizontal cylinders would suggest that if q/θ for any given hot body in a given fluid is plotted against θ , or any convenient function of θ , then the intercept will depend only on the geometry of the body concerned and the thermal conductivity of the fluid in which it is immersed. The slope, measured at some convenient point, will be a measure of the convective modulus of the fluid. As a first

experimental test of the validity of such a generalization measurements were taken of the heat losses from cylinders at a series of different orientations from horizontal to vertical. The intensity of the convection currents are expected

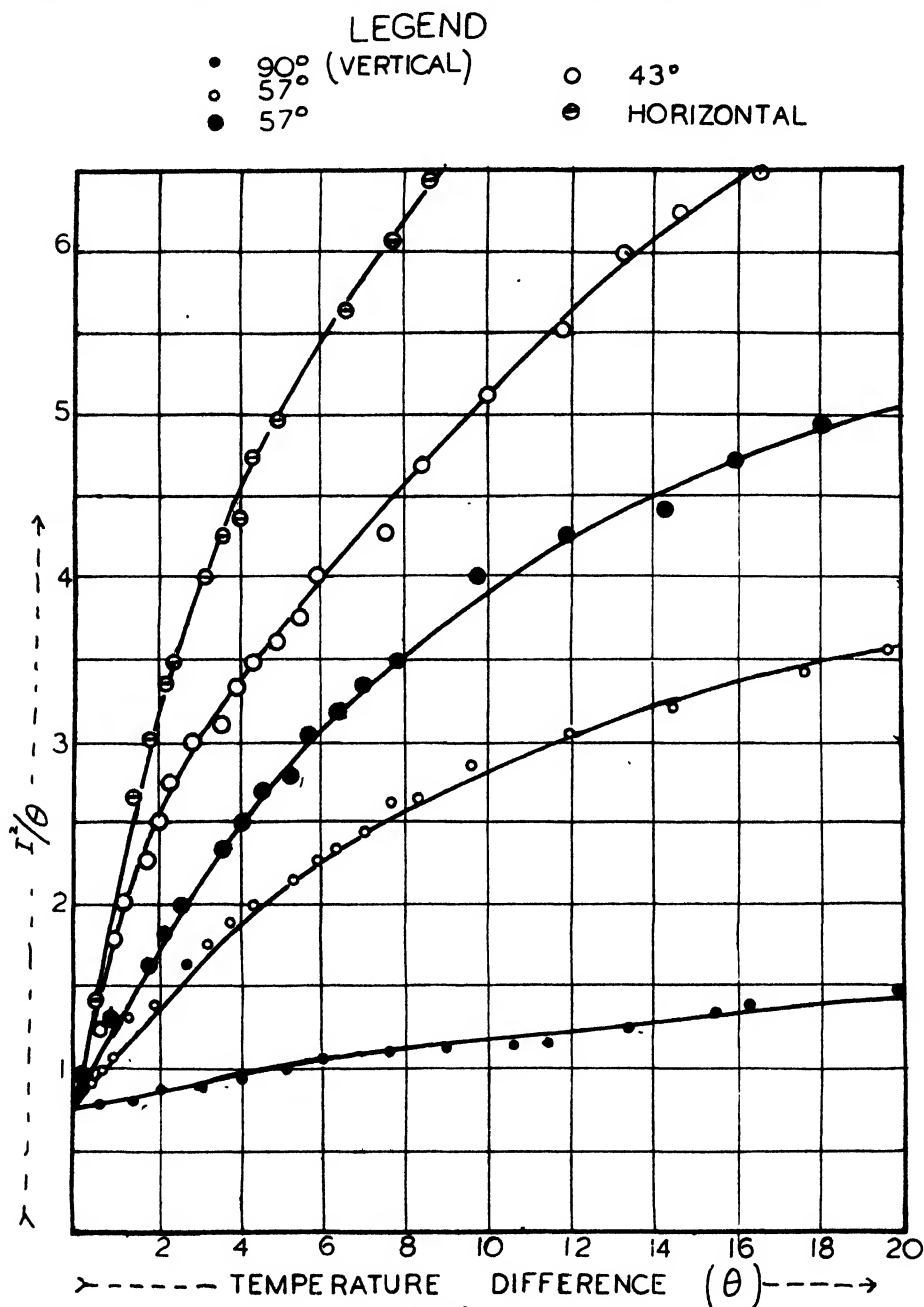


Fig. 1.

to be a maximum when the cylinder is horizontal and a minimum when vertical, so that the slopes of the q/θ versus θ curves are expected to decrease steadily as the heated cylinders are turned from the horizontal to the vertical position. However, the intercepts, if they really represent the thermal conductivity of the fluid concerned are expected to be unaffected by the orientation.

Figure 1 shows q/θ versus θ data taken from a heated cylinder consisting of a length of nichrome wire 2.7 cms. long and 0.0315 cm. diameter immersed in distilled water at 26.2° C. and heated by an electric current which was increased steadily from 0.2 to 3.5 amps. for each orientation. The temperature excess (θ) was measured by means of a fine tungsten-nickel thermocouple welded to the centre of the resistance wire. The various I^2/θ versus θ curves shown in Figure 1 refer to orientations (α) of 0°, 43°, 57°, 73° and 90° measured from the horizontal. It appears clear from Figure 1 that the curves, although showing very different "slopes", all have, within experimental error, a common intercept on the I^2/θ axis. The "slopes" are the steeper the more nearly horizontal the wires. The relative "slopes" have been measured by measuring the relative ordinates (in excess of the intercept) at a number of different abscissæ and averaging. The "slopes" compared with the cosines of the angles (α) of inclination to the horizontal are given in Table I. It appears therefore that the magnitude of the convective heat loss is roughly proportional to the horizontal projected area.

TABLE I.

Variation of Convective Heat Loss in Distilled Water with Inclination (α) to the Horizontal.

"Slope" of the I^2/θ v. θ Curves Relative to Horizontal Wire.	Cos α .
1.00	1.00
0.67	0.73
0.47	0.54
0.30	0.29
0.05	0.00

A further series of experiments were carried out on the same wire immersed in a 92.2% solution of glycerol in water at 23° C. Glycerol has about half the thermal conductivity of water but a very much lower convective modulus—mainly on account of the high viscosity. The curves shown in Figure 2 refer to measurements at inclinations of 0°, 45°, 56°, 80° and 90° to the horizontal. The curves are very much less steep than the corresponding curves for water; but again it will be observed that the curves all give a common intercept on the I^2/θ axis, which may therefore be taken as a measure of the thermal conductivity of glycerine. The slopes, measured in the same way as above, are given in Table II.

TABLE II.

Variation of the Convective Heat Loss in Glycerine with Inclination (α) to the Horizontal.

"Slope" of the I^2/θ v. θ Curves Relative to that of Horizontal Wire.	Cos α .
1.00	1.00
0.68	0.71
0.52	0.56
0.14	0.17
0.08	0.00

The difference in the rate of convective heat losses from horizontal and vertical cylinders, apparent from the results of a number of observers, has been the object of comment by Carne (1937), who points out, in particular, that the variation of heat loss with diameter shows the same form in the two cases.

LEGEND

- | | | | |
|---|----------------|---|------------|
| ● | 90° (VERTICAL) | ○ | 45° |
| ○ | 80° | ○ | HORIZONTAL |
| ○ | 56° | | |

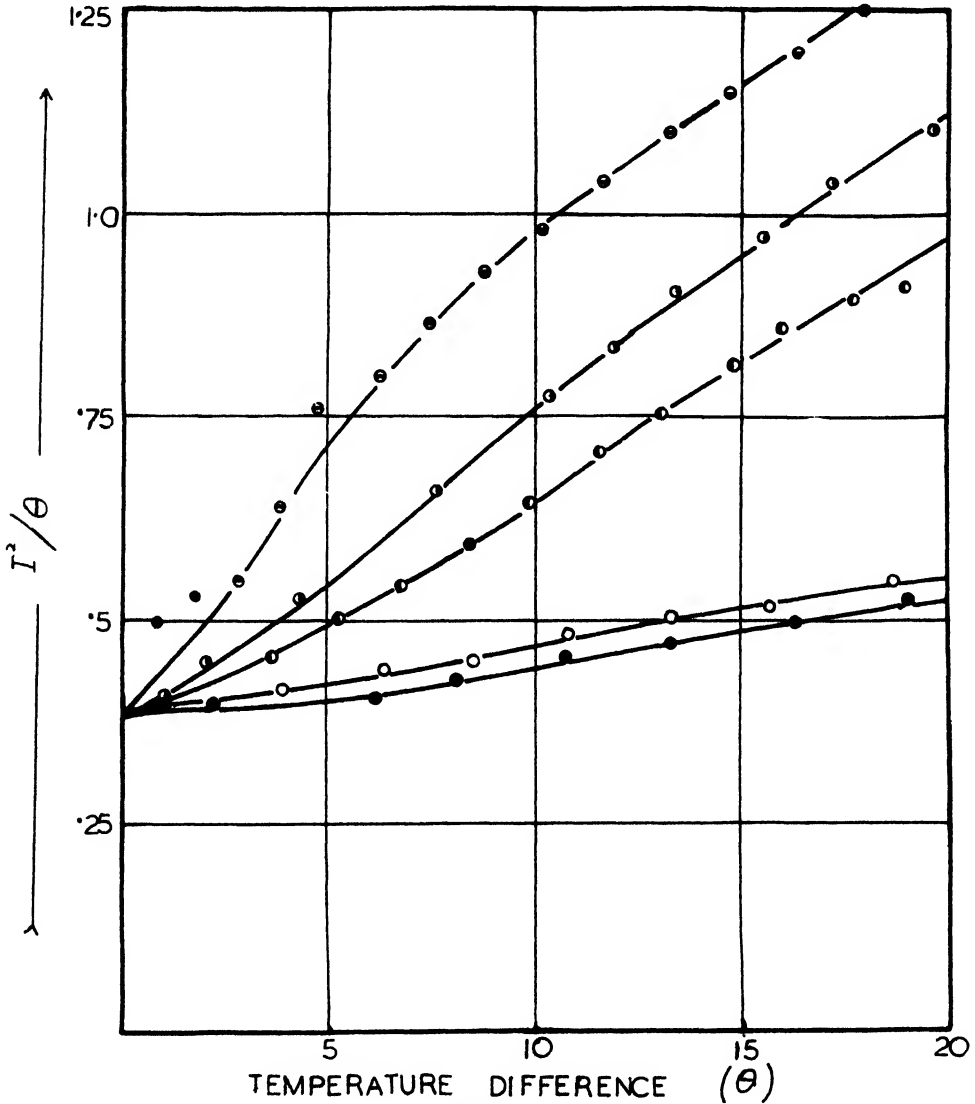


Fig. 2.

Figures 1 and 2 may be used to extend this observation. The curves for the heat losses at different orientations all have the same shape. The relationships between the rate of heat loss and the product of the Grashof and Prandtl numbers, applying to heated cylinders at different orientations, can be represented by functions of the same type differing only in the magnitude of the constants.

THE COMPARISON OF THE THERMAL CONDUCTIVITIES OF VARIOUS FLUIDS.

The equipment used for comparing the thermal conductivities of different fluids consisted of a single heated wire 4.5 cms. in length of 19 B & S gauge nichrome IV wire having a resistance of 0.074 ohm. To the centre of this there was welded a 34 gauge copper-constantan thermocouple. The resistance wire,

LEGEND

○ WATER	• ETHYLENE GLYCOL
● METHANOL	● 92% GLYCEROL
● 96% ETHYL ALCOHOL	⊕ CARBON TETRACHLORIDE
● ACETONE	⊗ CHLOROFORM
● ETHYL ACETATE	+ FORMIC ACID

○ AIR

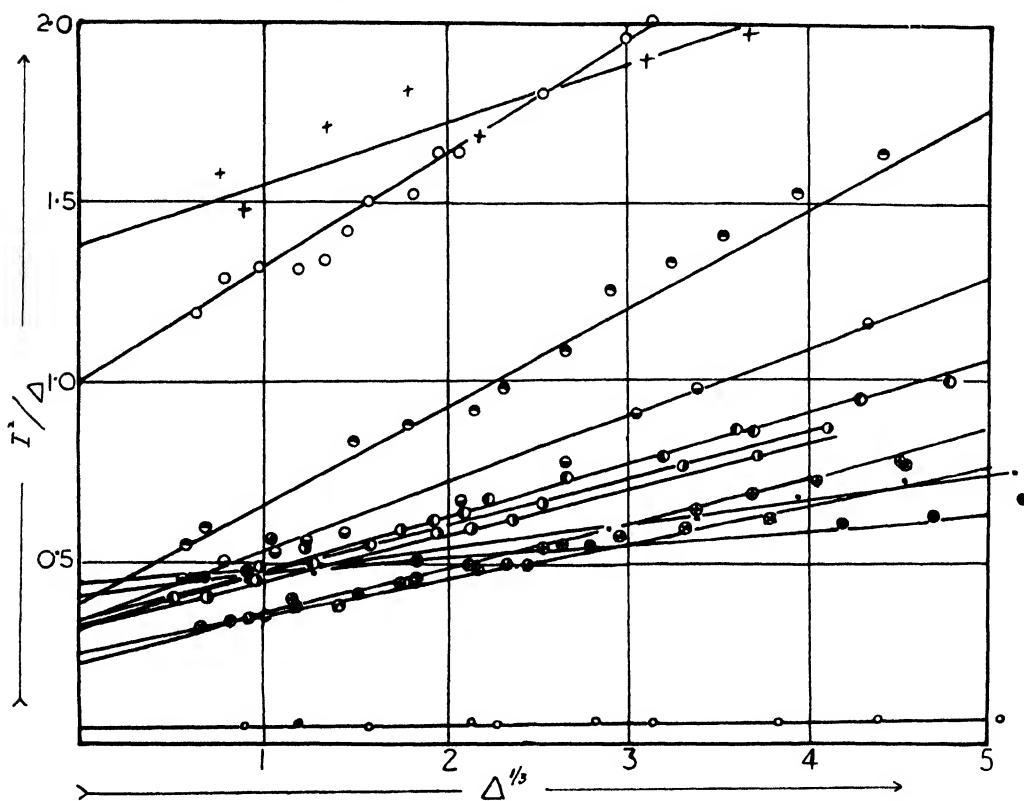


Fig. 3.

immersed in the fluid under test, was heated by A.C., the current being varied in the range from 0.2 to 20 amps. The lower limit with any given fluid being set by that giving the minimum measurable temperature rise as detected by the thermocouple, and the upper limit, in the case of a liquid, by that which just fails to produce boiling on the wire. The thermocouple was connected through a suitable shunt to a Cambridge Spot galvanometer, one division on the scale of which corresponded to a temperature rise of 0.336° C.

The first liquid to be examined was distilled water at room temperature (27° C.). Readings were taken of the current (I) versus galvanometer reading

(Δ) (proportional to the temperature rise θ). Then were examined in order: toluene, benzene, acetic anhydride, 95% acetic acid, formic acid, a check reading on water, methanol, 92% glycerine, 96% ethyl alcohol, ethyl acetate, carbon tetrachloride, air, water, ethylene glycol, acetone, chloroform and carbon disulphide. In these experiments duplicate runs were quite satisfactory.

LEGEND

- | | |
|---------------|---------------------|
| ● ACETIC ACID | ● ACETIC ANHYDRIDE |
| ● BENZENE | ● CARBON BISULPHIDE |
| ● TOLUENE | ○ WATER |

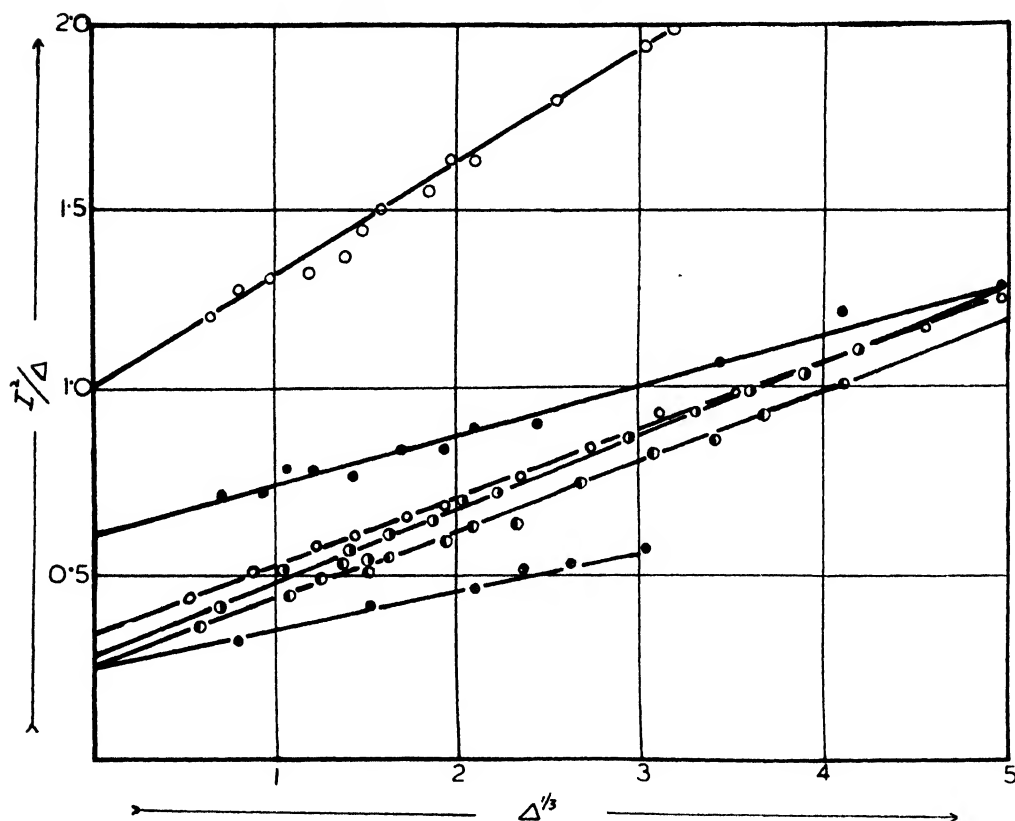


Fig. 4.

In the list of fluids above the one with the lowest thermal conductivity was the only gas examined—air. Any necessary correction for heat loss by radiation would therefore be most serious in this case. The value of the convective heat transmittance $h = q/\theta$ will be at its lowest at the lowest value of θ . The minimum value h_0 of h is by equation (3)

$$\frac{h_0 d}{k} = 0.40 \dots \dots \dots (5)$$

or

$$h_0 = 4k$$

since $d = 0.1$ cm.

Since the thermal conductivity of air at 300°K. is 5.8×10^{-5} Cals. cms. $^{-1}$ sec. $^{-1}$ $^{\circ}\text{C.}^{-1}$, the lowest value of the convective transmittance with which we will be concerned will be 23×10^{-5} Cals. cms. $^{-2}$ sec. $^{-1}$ $^{\circ}\text{C.}^{-1}$. Radiative transmittance is given by

$$h_r = 4\epsilon\sigma T^3$$

where ϵ is the emissivity and σ the Stefan-Boltzmann constant. For the emissivity of bright nichrome at 300°K. we take a value 0.08 (the average of metals similar to nichrome as regards to spectral emittance as given by Amer. Inst. Phys. (1941)). The radiative heat transmittance is thus computed to be

$$h_r = 1.2 \times 10^{-5} \text{ Cals. cms.}^{-2} \text{ sec.}^{-1} \text{ }^{\circ}\text{C.}^{-1}$$

and accordingly the radiative heat loss amounts to only 5% of the convective in the case of air and is a still smaller fraction in all the liquid media. We are justified therefore in ignoring radiative heat loss in these experiments.

From the experimental data obtained as outlined above the values of I^2/Δ (proportional to q/θ) were given as a function of Δ (proportional to θ). A suitable form for presenting the data, as indicated by equation (3) above would be a plot of I^2/Δ versus $\Delta^{1/3}$. The experimental data presented in this way are given in Figures 3 and 4 in which the attached legends indicate the fluids to which the points refer. It will be noted that the points fall on straight lines, each giving a positive intercept on the I^2/Δ axis. The intercepts for each fluid studied measured relative to water at 27°C. are given in Table III.

TABLE III.

Relative Intercepts of the I^2/Δ versus $\Delta^{1/3}$ Lines.

Substance.	Relative Intercept.	Relative Thermal Conductivity.
Water	1.00	1.00
96% Ethyl alcohol	0.31	0.30
Ethylene glycol	0.42	0.44
92% Glycerine	0.47	0.48
Methanol	0.36	0.35
Formic acid	1.28	—
Acetic acid 95%	0.34	0.29
Acetic anhydride	0.61	—
Acetone	0.29	0.30
Ethyl acetate	0.28	0.28
Benzene	0.28	0.26
Toluene	0.25	0.24
Carbon tetrachloride	0.21	0.28
Chloroform	0.25	0.23
Carbon bisulphide	0.25	0.26
Air.	0.041	0.040

Data for the relative thermal conductivities were obtained from the International Tables, the appendix of McAdams (1941) and from Keyes and Deem (1942). It will be observed from Table III that there is, in general, excellent agreement between the figures obtained by the present method and those which earlier had been accepted as representing the best available from the well-established methods.

Three possible sources of trouble became apparent during the measurements which led to these results. (1) Too high an electrical conductivity in the liquid under test will result in error due to a short-circuiting of the thermocouple e.m.f.

A high electrical conductivity would therefore lead to a spuriously high figure for the thermal conductivity as measured by this method. The high figure recorded in Table III for the thermal conductivity of formic acid may therefore be false. (2) When very volatile liquids (such as acetone or chloroform) were under test difficulty was experienced in obtaining a reproducible zero due apparently to a chilling of the cold junction of the thermocouple by surface evaporation of the liquid. All trouble of this nature could be eliminated by proper screening from convection currents in the air, or, better, by total enclosure. (3) In the very viscous liquids (such as glycerine), the time taken for the thermocouple to attain equilibrium was greatly prolonged. In the more limpid liquids a steady reading was attained in 1 to 2 minutes after switching on the current. In glycerine, particularly at low heating currents, times of the order 30 to 60 minutes were necessary. At higher heating rates the temperature of the wire in glycerine settled down to a steady value more rapidly.

ESTIMATION OF RELATIVE CONVECTIVE MODULI.

The experimental results as shown in Figures 3 and 4 can also be used to give a measure of the convective moduli of the fluids concerned. These figures may be interpreted by postulating that the heat loss factor can be represented by an equation of the type

$$\frac{qd}{k\theta} = A + B(ad^{3/2}\theta)^{1/3} \dots\dots\dots (6)$$

where A and B may be taken as constants over the range of θ for which data are available. For a given hot wire d is also a constant and we have

$$q/\theta = A'k + B'k(a\theta)^{1/3} \dots\dots\dots (7)$$

The intercepts from the lines obtained by plotting q/θ versus $\theta^{1/3}$ are therefore

$A'k$ and the slopes $\left(\frac{d(q/\theta)}{d\theta^{1/3}}\right)$ are $B'ka^{1/3}$. The convective modulus is therefore

proportional to the cube of the ratio slope:intercept. But the convective modulus of any fluid is related to other physical properties by

$$a = \frac{gc\beta\rho^2}{\eta k} \dots\dots\dots (8)$$

and consequently may be computed from tables of these properties provided all are known. The quantity a usually varies rapidly with the temperature, increasing with a temperature rise in the case of a liquid and decreasing with a temperature rise in the case of a gas. For water at 27° C. a has the value

$$2.0 \times 10^4 \text{ cms.}^{-3} \text{ } ^\circ\text{C.}^{-1}.$$

Experimental values for the various liquids tested compared with calculated values are given in Table IV as "relative convective moduli" or as a ratio of the convective moduli of the fluids concerned to that of water, both at 27° C.

Bearing in mind the fact that a 5% error in both the intercept and slope can lead to a 30% error in the measured convective moduli; there is, in most instances, excellent agreement between the measured and calculated convective moduli in Table IV. However, the agreement in the case of formic acid (of somewhat higher electrical conductivity than the other liquids studied) is not good; nor is it satisfactory in the case of the more volatile liquids, acetone, ethyl acetate, chloroform and carbon tetrachloride.

Summarizing the results of the last two sections, therefore, it appears that the method as suggested in this paper is capable of yielding accurate comparative figures for the thermal conductivities and convective moduli of liquids which are

TABLE IV.
Relative Convective Moduli at 27° C.

Fluid.	Relative Convective Moduli.	
	By Measurement.	By Computation from Physical Properties.
Water	1.00	1.00
96% Ethyl alcohol	6.3	6.3
Ethylene glycol	0.20	0.22
92% Glycerine	0.014	0.022
Methanol	10.6	9.3
Formic acid	0.14	1.4
Acetic acid 95%	7.8	5.6
Acetic anhydride	0.26	—
Acetone	6.5	18.0
Ethyl acetate	3.8	17.0
Benzene	9.5	10.0
Toluene	9.3	9.8
Carbon tetrachloride	7.3	15.0
Chloroform	3.0	16.0
Air.. .. .	0.003	0.005

not electrical conductors and are not too volatile. The method particularly commends itself to the comparison of the conductive and convective properties of binary mixtures and solutions of non-electrolytes.

COMPARISON WITH THE METHOD OF HUTCHINSON.

E. Hutchinson (1945) has proposed a hot-wire method for measuring the thermal conductivities of liquids based on one used by Bolland and Melville (1937) for the thermal conductivities of gases. Hutchinson uses a fine coiled coil filament axially in a narrow tube of the liquid under test. The wire is heated by a current of the order of 10 milliamps. and the measured temperature rise is only of the order of 1° C. Absolute values of the thermal conductivity may be calculated from the formula

$$q = \frac{\theta}{r} k \log r_1/r \dots\dots\dots (9)$$

where r is the radius of the wire and r_1 of the vessel.

Application of this equation assumes that convection currents are absent or that the Grashof numbers are small. There are three factors contributing to make this so. The temperature rise θ is low, the wires are fine, and they are used in the vertical position. Reference to Figures 1 and 2 above shows how very much less are the effects of convection from vertical as opposed to horizontal wires. As a matter of interest Hutchinson remarks that his results are erratic when the vessel is inclined at more than 25° to the vertical.

The method suggested in this paper differs from that of Hutchinson by the absence of near walls at a fixed temperature and by the measurement of a temperature difference between the surface of the wire and the bulk of the fluid. Comparison of equation (9) with the limiting form (equation 5) expressed in the form

$$q = 0.40 \frac{\theta k}{2r} \dots\dots\dots (5a)$$

may be used to give a measure to the thickness of the stagnant Langmuir film around the heated wire at low Grashof numbers. From a comparison of (9) and (5a) it follows that the effective external radius of the stagnant film is given by

$$\log_e r_{1,r} = 0.20$$

$$\text{or} \quad r_1 = 1.221r \dots\dots\dots (10)$$

SUMMARY.

A length of resistance wire is immersed in a fluid and heated by a current I . The heat input is proportional to I^2 and the temperature difference (θ) between bulk of fluid and the wire may be measured by means of a small thermocouple attached to the centre of the heated wire. When from data thus obtained I^2/θ is plotted against $\theta^{1/3}$ straight lines are obtained, the intercepts on the I^2/θ axis of which are proportional to the thermal conductivities of the fluids concerned while the ratios of the slopes to the intercepts are proportional to the cube root of the convective moduli.

The method is tested experimentally by measurements in fluids of known thermal conductivities and convective moduli. The results obtained show satisfactory agreement except from liquids of high electrical conductivity (resulting in short-circuiting of the thermocouple), or too high a volatility (which results in a cooling of the c.j. of the thermocouple).

The method has also been tested by drawing the I^2/θ versus θ curves for a number of different orientations of the wire in the one fluid. The curves obtained are similar in shape and have a common intercept and a slope which is a maximum when the wire is horizontal and a minimum when the wire is vertical.

The magnitude of the heat flow from a horizontal cylinder at vanishing temperature difference leads to a figure of $0.221 \times \text{radius}$ for the thickness of the stagnant film surrounding the cylinder.

It is suggested that the method outlined in this paper would be particularly valuable in a rapid assessment of the heat transfer properties of concentrated solutions of non-electrolytes.

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THE UNIFORM CONVERGENCE OF SEQUENCES OF MONOTONIC FUNCTIONS.

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(Communicated by PROFESSOR K. E. BULLEN.)

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The following result is due to G. Pólya*): If a sequence $f_n(x)$ of monotonic functions converges to a continuous function $f(x)$ in an interval $a < x < b$, then the convergence is uniform. It will be shown in the present paper that in the case of a discontinuous limit function $f(x)$ the uniform convergence can likewise be characterized in terms of ordinary convergence: the necessary and sufficient condition for uniform convergence is that both $f_n(x-0) \rightarrow f(x-0)$ and $f_n(x+0) \rightarrow f(x+0)$. More precisely:

If $f_n(x)$, $f(x)$ are defined and monotonic non-decreasing in $a < x < b$, then $f_n(x) \rightarrow f(x)$ uniformly in $a < x < b$ if and only if

- (1) $f_n(x) \rightarrow f(x)$ for all x of an everywhere dense set E in $a < x < b$ containing the set D of all discontinuity points of $f(x)$

and

- (2) $f_n(x-0) \rightarrow f(x-0)$, $f_n(x+0) \rightarrow f(x+0)$ for all x in D .

Proof.

1. Let $f_n(x) \rightarrow f(x)$ uniformly. (2) only has to be proved. Actually (2) holds uniformly in $a < x < b$: to any $\varepsilon > 0$, $N(\varepsilon)$ exists such that

$$|f(t) - f_n(t)| < \varepsilon \text{ for } n > N \text{ and } a \leq t \leq b,$$

whence

$$\lim_{t \rightarrow x \pm 0} |f(t) - f_n(t)| = |f(x \pm 0) - f_n(x \pm 0)| \leq \varepsilon.$$

2. Let (1), (2) hold. It will first be shown that (1), (2) hold for all x in the interval. As (1), (2) hold on D it is sufficient to consider the continuity points of $f(x)$. Let x be a continuity point.

To any $\varepsilon > 0$, t_1, t_2 exist in E such that $t_1 < x < t_2$ and

$$f(x) - \frac{\varepsilon}{2} \leq f(t_1) \leq f(t_2) \leq f(x) + \frac{\varepsilon}{2}.$$

By (1), N exists such that

$$|f(t_i) - f_n(t_i)| < \frac{\varepsilon}{2} \text{ for } n > N, i=1, 2.$$

Hence

$$f(x) - \varepsilon \leq f_n(t_1) \leq f_n(x-0) \leq f_n(x) \leq f_n(x+0) \leq f_n(t_2) \leq f(x) + \varepsilon,$$

whence

$$\lim_{n \rightarrow \infty} f_n(x-0) = \lim_{n \rightarrow \infty} f_n(x) = \lim_{n \rightarrow \infty} f_n(x+0) = f(x) = f(x-0) = f(x+0).$$

* Ueber den zentralen Grenzwertsatz der Wahrscheinlichkeitsrechnung und das Momentenproblem, *Mathematische Zeitschrift* 8 (1920), pp. 171-181.

It will now be shown that the assumption of non-uniform convergence leads to a contradiction. In the case of non-uniform convergence, $\epsilon > 0$, a sequence of integers $n_1 < n_2 < n_3 < \dots$ and a sequence of real numbers x_1, x_2, x_3, \dots in $a < x < b$ exist such that

$$(3) \quad |f(x_k) - f_{n_k}(x_k)| > \epsilon \text{ for } k=1, 2, 3, \dots$$

The x_k have at least one limit point t in the interval, and it may be assumed that $x_k \rightarrow t$. At most a finite number of the x_k can be equal to t ; for, by (1), $f_n(t) \rightarrow f(t)$, i.e. $|f(t) - f_n(t)| < \epsilon$ for $n > N$, and (3) shows that $x_k \neq t$ for $n_k > N$. Hence, an infinite subsequence of the x_k exists whose terms are either all less or all greater than t . It is sufficient to consider the first case. Choosing $\delta > 0$ such that

$$0 < f(t-0) - f(t-\delta) < \frac{\epsilon}{2},$$

K exists such that

$$t - \delta < x_K < t, \quad |f(t-\delta) - f_{n_K}(t-\delta)| < \frac{\epsilon}{2}, \quad \text{and} \quad |f(t-0) - f_{n_K}(t-0)| < \frac{\epsilon}{2},$$

whence

$$\begin{aligned} f(x_K) - f_{n_K}(x_K) &\leq f(t-0) - f_{n_K}(t-\delta) \\ &= f(t-0) - f(t-\delta) + f(t-\delta) - f_{n_K}(t-\delta) < \epsilon, \end{aligned}$$

and

$$\begin{aligned} f(x_K) - f_{n_K}(x_K) &> f(t-\delta) - f_{n_K}(t-0) \\ &= f(t-\delta) - f(t-0) + f(t-0) - f_{n_K}(t-0) > -\epsilon \end{aligned}$$

which contradicts (3).

Pólya's result is a corollary, as for continuous $f(x)$ condition (2) is vacuous.

The result may be extended to sequences $f_n(x)$ which are defined for $-\infty < x < \infty$ and converge to a bounded function $f(x)$. Using a transformation like $x = \tan y$, and applying the above result to the interval $-\frac{\pi}{2} < y < \frac{\pi}{2}$, it is seen that the only additional condition required is

$$\lim_{n \rightarrow \infty} \left(\lim_{x \rightarrow \pm \infty} f_n(x) \right) = \lim_{x \rightarrow \pm \infty} f(x).$$

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July, 1947.

A METHOD OF DETERMINING THE DISTRIBUTION OF OIL IN A RESERVOIR ROCK BY MEANS OF ULTRA-VIOLET LIGHT.

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Manuscript received, June 26, 1947. Read, August 6, 1947.

INTRODUCTION.

The fluorescent properties of both crude and refined oils under ultra-violet light are well-known and have been used in petroleum technology in America and Germany. The value of ultra-violet light in the preliminary examination of drill cores to detect the presence of oil has also been appreciated but there is apparently no record in oil literature of the use of ultra-violet light to determine the detailed distribution of oil in a reservoir rock.

In 1945 the author collaborated with Mr. R. F. Thyer, Geophysicist, in an investigation of the reservoir properties of portion of the oil-bearing glauconitic sandstone at Lakes Entrance, Victoria. The investigation included a detailed examination of drill cores from the reservoir rock and, subsequently, an inspection of the reservoir rock *in situ* in exposures at the bottom of the Lakes Entrance oil shaft. Ultra-violet light was used to determine the detailed distribution of oil in the rock, both in cores and *in situ*. As yet the author is not at liberty to disclose the results of the investigation, but the techniques adopted are described in this paper as they may be of interest to other workers.

It should be remembered, however, that this method of core analysis was developed to deal with a reservoir rock in which oil was, for the most part, invisible, and in very small quantities. The method has, therefore, a limited application in oil technology although it could be adopted to deal with reservoir rocks with different characteristics. Notes on the examination of the rock *in situ* are included for their interest rather than utility, since very few oil fields could present a geologist with such unique opportunities.

EXAMINATION OF DRILL CORES BY ULTRA-VIOLET LIGHT.

General.

During the investigation at Lakes Entrance a diamond drill hole, termed the "Shaft Bore", was drilled from the bottom of a shaft to penetrate a thickness of 19 ft. 2½ in. of the oil-bearing glauconitic sandstone. The glauconitic sandstone was cored in sections approximately 2 ft. long and 1½ in. in diameter. Each core was transferred directly from the core barrel to a special air-tight container and then taken to Canberra, where the cores were analysed.

Previous experience in drilling at Lakes Entrance indicated that some cores from the glauconitic sandstone, when first removed from the core barrel, carried brown oily patches on the surface which disappeared after exposure to the air. Furthermore, no oil could be detected by eye or by microscope when these cores were subsequently examined in the laboratory—presumably because the small quantity of oil present was in a finely divided state and could not be detected against the background of green glauconitic sandstone.

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Most of the cores of glauconitic sandstone from the Shaft Bore showed patches of oil on the surface when first removed from the core barrel and the position and extent of each patch were carefully logged because the oil appeared to indicate the position of oil-bearing sandstone. However, these patches were no longer visible when the cores were unsealed in the laboratory some weeks later and it was at this stage that ultra-violet light was first used. Its value was at once apparent, firstly as a means of relocating the oily patches on the surface of the cores and subsequently as a means of establishing the detailed distribution of oil in the sandstone.

Ultra-violet Light Equipment.

In the experimental stages the cores were examined under two types of ultra-violet lamp: the "Mineralight" lamp and the "Mercra" lamp. The "Mineralight" equipment consists essentially of a coiled quartz tube in which a cold electric discharge through mercury vapour takes place. Electric power may be obtained either from batteries or from the 240 volt A.C. main supply with suitable transformer. The lamp is rated at 30 watts and is fitted with a filter constructed from a type of glass known as "Red Purple Corex A No. 986". The ultra-violet light emitted mostly corresponds to a wave-length of 2537 Å.

The "Mercra" lamp provides a source of near ultra-violet light and no appreciable amount is emitted below a wave-length of about 3100 Å. The equipment consists of a mercury vapour lamp enclosed in a dark glass envelope, which absorbs most of the visible light. The lamp which was used is rated at 80 watts and, in association with a choke coil, operates from the 240 volt A.C. main supply.

Crude and refined oils fluoresce under both lights, but the fluorescence is distinctly brighter under the "Mercra" lamp, which was therefore used throughout the investigation. Under this lamp portions of the core which contain oil show a yellow to a pale yellowy-brown fluorescence, apparently dependent upon the proportion of the rock surface actually covered with oil and on the thickness of the oil films.

Several tests were carried out to ensure that this fluorescence was actually produced by crude oil in the core and not by any of the other substances known to be present. Glucose solution had been introduced into the drilling water as an index chemical and mercuric chloride and merthiolate solution had been used to inhibit fermentation of any glucose penetrating the cores. Each of these substances was tested under ultra-violet light and showed no fluorescence. Next a few fragments of fluorescent and apparently oil-bearing core were placed in a test tube stoppered with cotton wool. Neither tube nor stopper showed any fluorescence under ultra-violet light. The test tube was then heated for a few minutes, cooled, and both tube and stopper bore a condensate which gave a bluish-white fluorescence typical of oil distillates. The fragments of core were also examined after heating and found to have lost all fluorescence under ultra-violet light. A further experiment was carried out using "Shellite" solvent to remove oil from a portion of fluorescent core, and after drying at low temperature, the core no longer showed fluorescence. Finally a portion of the core showing no fluorescence was impregnated with Lakes Entrance oil and the resulting fluorescence was identical with that found elsewhere in the cores.

It should be noted that special spectacles with side shields were worn while using the lamp to protect the eyes from damage by concentrated ultra-violet light.

Procedure.

In the first series of tests carried out at Canberra the external surface of the cores were examined under ultra-violet light. The unbroken core was placed

horizontally in an adjustable core holder which allowed rotation of the core about its principal axis. The examination was carried out in the dark room and the cores were returned to their sealed containers as soon as possible.

Oily patches originally observed on the surface of the cores could be relocated under ultra-violet light and the distribution of fluorescent patches on the complete surface of the core was portrayed on three columnar sections, each being a projection on to a horizontal plane of one-third of the surface of the core.

The resulting core diagrams provided a clear picture of the distribution of oil on the surface of the cores. However, later work showed that these diagrams, although they indicated roughly the location of the principal oil-bearing zones, did not present a true picture of the original distribution of oil in the rock, because, in many cores, oil which had welled out of portion of a core during drilling and recovery had either gravitated down the surface of the core or had been spread by the core catcher over a larger area than it had originally occupied. The distribution of oil on the surface could also have been effected during handling or by movement within the containers.

This method was therefore replaced by one which dealt solely with unexposed sections of the core.

In the procedure finally adopted the cores were removed from the containers, cut into sections approximately 3 in. in length, and stored in small bottles with air-tight caps. This made handling easier and reduced the total period of time that cores were exposed to the air during examination. To enable these sections to be oriented a heavy pencil line was drawn longitudinally along the surface of the core before it was cut.

Each section examined was then cut into thin discs approximately $\frac{1}{4}$ in. in thickness by means of a special core cutter. This consisted of a pair of semi-circular steel chisels with a radius of curvature approximately the same as that of the core. The core was held in a vice and the chisels fitted over it to provide a disc of the correct thickness. The core could then be broken cleanly by one sharp blow with a hammer.

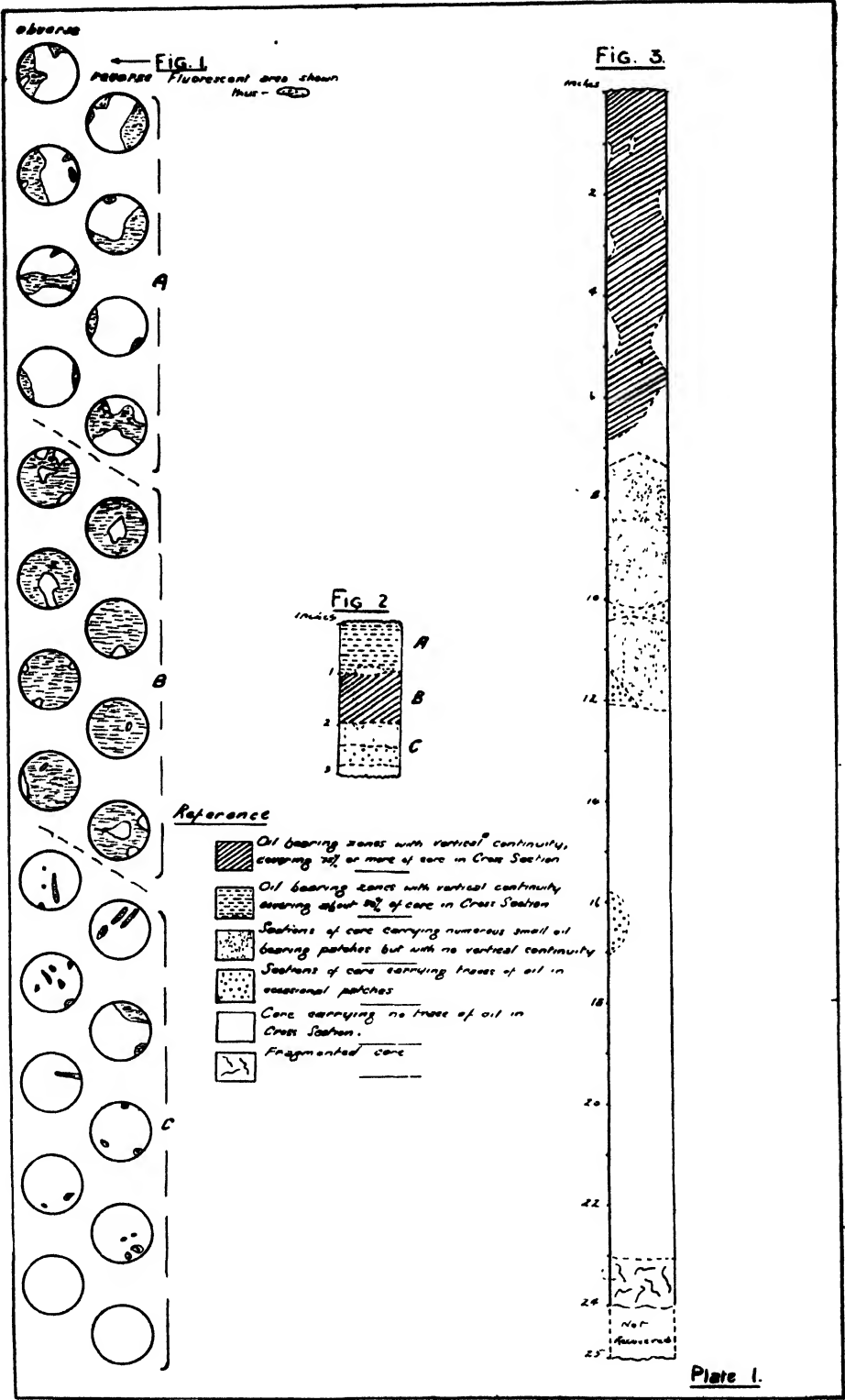
By means of the pencil line mentioned above, each disc cut from the core section could be placed in correct orientation. The suite of discs so obtained (10 to 12 discs for each 3 in. core section) was examined under ultra-violet light and fluorescent areas showing on each were plotted on a sheet bearing a series of circles representing cross-sections of the core at half natural size. Both obverse and reverse sides were examined to provide two series of diagrams from which the distribution of oil within the core could be established. Fluorescent patches on the discs were shown as stippled areas approximately to scale on the circular diagram but variations in the intensity of fluorescence were not depicted. A set of diagrams representing 3 in. of core are shown in Figure 1.

The fluorescent pattern was then examined to determine—

- (a) The general distribution of oil in cross-section.
- (b) The approximate percentage of cross-sectional area showing oil.
- (c) Whether oil-bearing patches had vertical continuity through two or more discs.

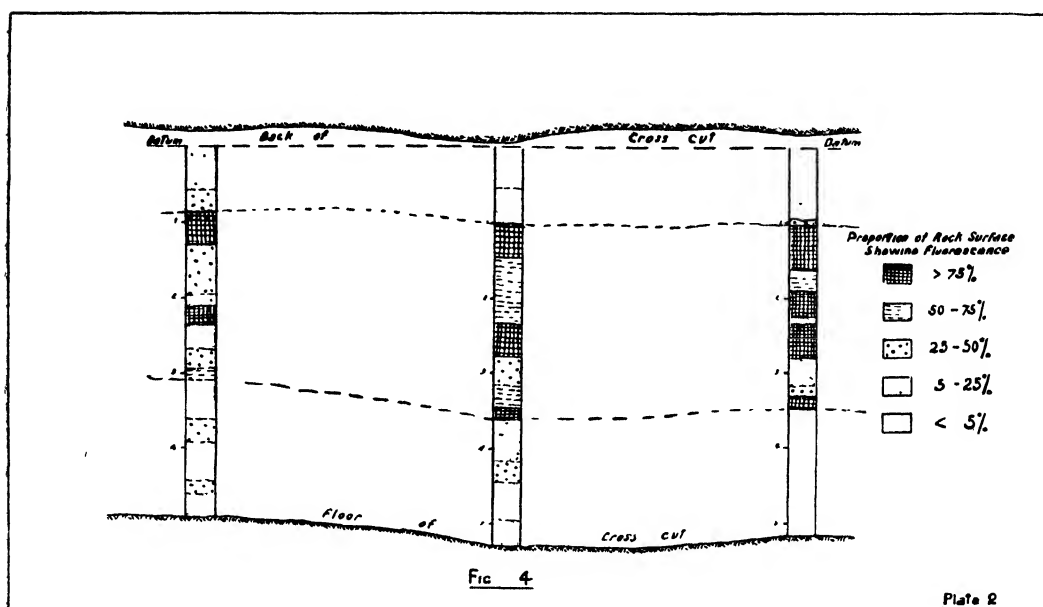
The core section could then be classified into one or more of the following five grades :

- (1) Oil-bearing patches covering 75 per cent. or more of the core in cross-section and with vertical continuity.
- (2) Oil-bearing patches covering approximately 50 to 75 per cent. of the core in cross-section and with vertical continuity.
- (3) Sections of core carrying numerous small oil-bearing patches with no vertical continuity.
- (4) Sections of core carrying a few oil-bearing patches.
- (5) Core carrying no oil in cross-section.



Finally this information was transferred to a columnar section on half natural vertical scale (Figure 2). This section was taken to represent a vertical plane passing through the centre of the core and the distribution of oil in the core, as established from the discs, was projected somewhat diagrammatically thereon. By this method a columnar section was constructed for each of the cores examined and one of these completed core diagrams is shown in Figure 3. More elaborate methods of portrayal, such as three-dimensional diagrams, could readily be devised, but where a large number of cores is involved a simple means of portrayal is important.

A generalized columnar section of the whole 19 ft. 2 in. of sandstone penetrated was then prepared from these individual columnar sections using a



simplified classification which divided the sandstone into major oil-bearing zones, minor oil-bearing zones, sandstone carrying isolated patches of oil and sandstone carrying no trace of oil.

Ultra-violet light examinations were followed by tests to determine the percentage oil saturation and these closely confirmed the quantitative work described above. The delineation of oil-bearing patches of sandstone by ultra-violet light also aided in petrological work and the essential difference between oil-bearing and barren rock could be determined. Ultra-violet and ordinary electric lights were arranged over a microscope in a dark room. Discs cut from the cores were placed on the microscope stage, and barren and oil-bearing portions compared after they had been defined by ultra-violet light.

USE OF ULTRA-VIOLET LIGHT UNDERGROUND.

The oil-bearing sandstone at Lakes Entrance does not outcrop, but in November, 1945, a winze sunk from the bottom of the oil shaft penetrated approximately 15 ft. into this formation and provided the first opportunity of examining the rock *in situ*.

Ultra-violet light was again used in a series of detailed examinations to delineate the oil-bearing portions of the rock. It was not possible to use the

" Mercra " lamp for this work since it was not adapted to operate from batteries, so a " Mineralight " was employed and powered from a 6-volt car battery.

Since oil was oozing from numerous patches in the section of rock exposed, the whole surface of the rock became covered with oil and care had to be taken to prepare a clean section for examination. A vertical channel about 6 in. wide and 1 in. to 2 in. deep was picked in the sandstone. A measuring tape was suspended from a nail inserted at a datum point at the top of the channel and the section then examined under ultra-violet light. The light was operated by an assistant while the observer logged the channel into sections and estimated the percentage area of fluorescence in each section. Short cross-cuts were eventually driven in the uppermost beds of the sandstone and vertical sections were cut and examined every 4 ft. along the walls and faces of the cross-cuts. Each vertical section was plotted to scale in the office and from the individual observations longitudinal sections and cross-sections of the workings were constructed to provide a clear picture of the distribution of oil in the rock. Three of these vertical sections are reproduced in Figure 4.

The distribution of oil established by this work agreed within very close limits with that already determined from the diamond drill cores in the same section of rock. Thus the underground work constituted a valuable check on the veracity of the earlier determinations which were based on the cores from a single drill hole.

ACKNOWLEDGMENTS.

The writer is indebted to Mr. R. F. Thyer for many helpful suggestions during the original investigation and for his criticism of this paper. Thanks are also accorded to the Director of the Bureau of Mineral Resources, Dr. H. G. Raggatt, for his permission to publish the work.

SPECTROSCOPIC CHARACTERISTICS OF ORDINARY ACHESON GRAPHITE.

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INTRODUCTION.

This report considers the suitability of ordinary low-grade Acheson graphite for spectrographic electrodes. The characteristics investigated were purity and homogeneity. Attempts to purify the graphite by chemical treatment are also reported.

The main point of this paper is a quantitative statement of results in terms of relative intensities of impurity lines before and after treatment. In the past there has been a considerable divergence of opinion among spectrochemists as to what constitutes an "adequate" purification process.⁽¹⁻¹⁰⁾ The use of various kinds and qualities of graphite and carbon differing widely in natural purity, together with the lack of quantitative data, has made a proper comparison of methods of purification impossible.

In attempting to avoid these difficulties, results have been (1) stated quantitatively, both as regards average intensities of impurity lines and also probable deviations from the average, (2) compared with Hilger H.S. brand graphite, which is accepted as suitable for most spectrographic analysis. (It should be emphasized that in making comparison with Hilger graphite absolutely no reflection is intended on the manufacturers of Acheson graphite. The Acheson brand tested is a low-grade one certainly never intended for spectroscopic use. It is very cheap in comparison with Hilger H.S. brand, which is supplied specifically for spectroscopy.)

All spectrograms were taken with a Hilger E179 one-metre quartz spectrograph and densities measured with a Zeiss microphotometer.

PURITY.

Specially purified graphite rods can be purchased from several manufacturers. These are usually expensive and were also in very short supply in Australia during the war, facts which obliged the writer to consider using ordinary Acheson graphite whenever possible.

$\frac{1}{4}$ in. and $\frac{3}{8}$ in. diameter Acheson rods were examined. These were broken to $\frac{5}{8}$ in. lengths and the broken faces arced at 10 amps.

As most of the analytical work of this laboratory has been confined to the spectral region 5000–2000 Å.U., the rods were examined only in this range. Elements detected were Ca, Cu, Ti, V, Al, Si, Mg, Fe, B. All of these could also be detected in the Hilger graphite. Both sizes of each type are included as there is some indication that the larger size is purer.

One line representative of each impurity element has been measured in density relative to background for each spectrum considered. For the purpose of comparison the intensity of each line has been taken as unity for the $\frac{1}{4}$ in. Acheson rods, relative intensities for the other three rods being found by conventional methods of photographic photometry. Figures quoted in Table 1

are average intensities based on 10 arcings for each type of rod. Intensities are measured always for light from the arc column. Some figures for Hilger rods are very doubtful, these lines being barely distinguishable against the background and on the limit of sensitivity of the microphotometer.

TABLE 1.

Element.	Wave-length. V.U. (M.I.T.).	A. Acheson ½ in.	B. Acheson ½ in.	C. Hilger ½ in.	D. Hilger ½ in.	E. Acheson ½ in. 3-day HCl.	F. Acheson ½ in. 1-day HNO ₃ .	G. Acheson ½ in. 4-day HNO ₃ .
Ca	4226.728	1.00	0.81	1.12	0.54	0.2	0.6	0.3
Cu	3247.540	1.00	0.81	0.72	0.58	0.7	0.7	0.6
Ti	3234.52	1.00	0.82	0.49	0.36	0.6	0.5	0.4
V	3102.299	1.00	1.2	0.74	0.72	0.7	0.8	0.6
Al	3082.155	1.00	0.68	0.49	0.47	0.6	0.7	0.5
Si	2881.578	1.00	1.1	0.51	0.22	1.0	0.9 (?)	1.0
Mg	2852.129	1.00	1.78	4.47	0.36	0.5	0.5	0.3
Fe	2599.39	1.00	0.69	0.29	0.28	0.3	0.6	0.3
B	2497.733	1.00	1.2	1.2	1.0	1.5 (?)	1.3 (?)	1.4 (?)

The relative impurity of the Acheson rods is evident from these figures. In particular, the difference in the degree of development of the iron spectrum corresponding to intensities 1.0 and 0.28 is considerable at this level of intensity, affecting very seriously the use of this Acheson graphite for analytical purposes.

HOMOGENEITY.

Repeated arcings showed that Acheson rods were very inhomogeneous. The better rods compared favourably with Hilger rods, while the worst gave well-developed spectra of all the above elements.

On the other hand, Hilger rods prepared for arcing in exactly the same way always gave similar spectra as regards most elements, so that the impurity was not due to chance contamination in the laboratory of occasional rods.

This is expressed in Table 2, which compares Acheson and Hilger ½ in. rods. Individual intensities (I_1, I_2, \dots, I_{10}) of the same 10 arcings were calculated and the probable deviation ΔI from the mean \bar{I} of a single arcing calculated by

$\Delta I = \pm 0.67 \sqrt{\frac{\sum_{i=1}^{10} (\bar{I} - I_i)^2}{9}}$. To emphasize the difference mean intensities were corrected to unity for both types.

TABLE 2.

Element.	Acheson ½ in.	Hilger ½ in.
Ca	1.00 ± 0.15	1.00 ± 0.12
Cu	0.15	0.22
Ti	0.51	0.10
V	0.24	0.11
Al	0.22	0.02
Si	0.21	0.16
Mg	0.18	0.15
Fe	0.57	0.05
B	0.14	0.09

Some elements are obviously quite unpredictable in Acheson rods, especially Fe. Hilger rods are less reliable only as regards copper. Occasional rods show copper lines moderately intense. Danger of contamination was very slight, in fact the Hilger rods were kept in their original packing until the time of use. In all these experiments they were broken to correct lengths (not machined in any way) and the broken surfaces arced.

The inhomogeneity is really more serious than the impurity itself. Rods of known state of purity can often be used in spectroscopic work by photographing the blank spectrum alongside. With Acheson rods a blank spectrum would be useless, as it would represent only the tip of the rod actually burned during the exposure. A pocket of impurity lying below the surface would be exposed by continued arcing. This sort of thing has in fact been observed repeatedly. So-called "jumping plate" spectra were taken, i.e. the plate-holder was racked at regular intervals of time while the arc burned.

Figure 1 shows some curious results obtained in this way. These are plots of line density relative to background, against burning time. All plots are from the same plate and hence show simultaneous behaviour of the elements. A quite striking feature is the correspondence between certain elements, viz. Ti, V, Al, Si. (Ca, Fe, Mg may also be correlated with this group—other plates did not always confirm these, however.)

Presumably these impurities occur together in pockets due in some way to the method of manufacture of the graphite. Copper and boron seem generally to be unrelated to this scheme. All plates of Acheson graphite have shown this behaviour to a greater or lesser extent and the effect is believed to be real. Fluctuations observed in Hilger arcings were not large enough to observe any obvious correlation between impurity elements. Figure 1 shows Ca, Si, B only. There is a general trend due to fractional distillation in the arc removing the more volatile elements and concentrating B.

CHEMICAL PURIFICATION.

For operation on a small scale a pyrex extractor was ideal. This periodically refluxed the rods with distilled acid. Rods broken or cut to final form were placed in the extractor space. The various solvents placed in the lower reservoir were boiled by a gas ring or electric hot-plate regulated to cause the 500 c.c. soxhlet to reflux about every 30 minutes. Approximately 10 pairs of rods were treated at a time. One shortcoming of the soxhlet is that it tends to give unequal treatment due to the rods at the bottom of the pile being immersed longer while the liquid builds up to the siphoning level. During a prolonged treatment the condenser was removed at least twice per day and the electrodes stirred well with a silica rod.

After solvent treatment electrodes were boiled for several hours in successive washes of distilled water.

The scope of chemical treatment tried here has not been extensive and figures are given only for HCl and HNO₃. These solvents require only the simplest equipment and a minimum of attention and are much more agreeable to work with than H₂SO₄. The latter, with its high boiling point, requires the soxhlet to be lagged and also all sorts of precautions need to be taken as the rods tend to disintegrate during treatment.

To ensure that the chemical processes themselves were not introducing impurities the obvious precaution was taken of subjecting Hilger rods to the same treatment. These always emerged slightly improved as regards most elements, but never worse.

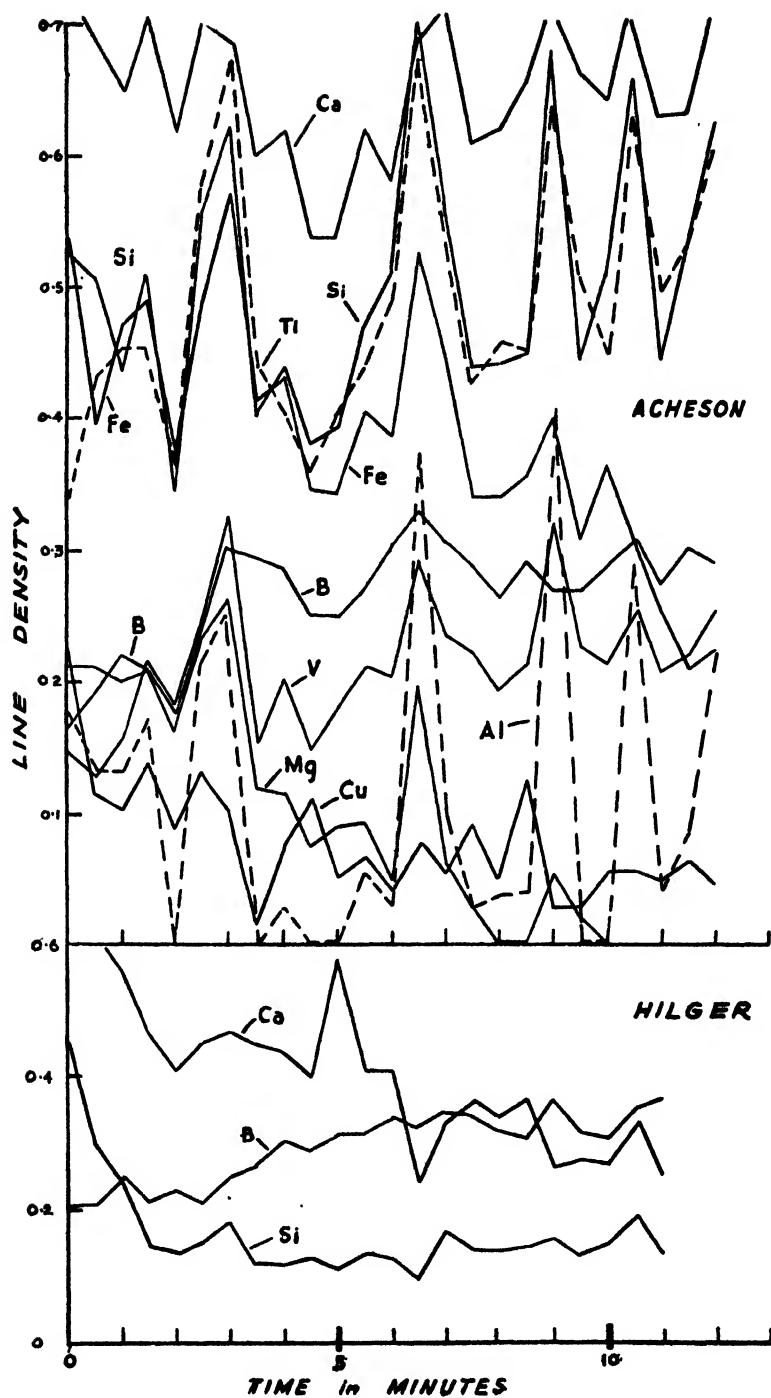


Fig. 1.

RESULTS.

Continuing the method of recording used in columns A and D of Table 1, i.e. taking the intensity with untreated Acheson graphite $\frac{1}{4}$ in. as unity intensity, the last three columns (E, F, G) give the intensities of impurity lines after chemical treatment with HCl (3 days) and HNO₃ (1 and 4 days). Averages from about 10 arcings are given in each case.

It is seen that an *average* purity similar to that of Hilger rods can be obtained for most elements (except B and Si) by either HCl or HNO₃ soxhlet treatment for 3-4 days. Such rods are still inhomogeneous and too unreliable for most work.

Uniformly reliable rods *never* exceeding the impurity of Hilger graphite require 12-15 days of either HCl or HNO₃ (neither acid seems to show any marked superiority for this purpose). This duration of the treatment results in average intensities of the order of 0.1, certainly superior to Hilger rods. These rods are highly satisfactory. The treatment is very lengthy but requires practically no supervision once in operation. Residual lines showing in occasional spectra are chiefly Fe, 2599.39, 2598.37; Ti, 3234.52, 3236.58, 3239.04, 3241.98; Mg, 2852.129 together with B, Si. Ca lines which are very persistent can usually be wholly removed by this treatment.

Aqua-regia does not significantly improve the figures quoted for HCl and HNO₃. None of the above chemical treatments adversely affects the final rods in any way.

H₂SO₄ is unsuited to the soxhlet method and boiling the electrodes in a flask requires a large number of washes to be effective and is very extravagant with acid. A few trials made here showed it to be more effective in removing Ti and V (Ti especially is a troublesome and irregular residual). No quantitative data have been accumulated for H₂SO₄ treatment. B and Si are present in both the Hilger and the Acheson graphite and are probably untouched by any acid treatment. Table 1 actually shows a rise in the B line intensity. This is almost certainly spurious, due to B carrying more of the electric arc when the more volatile elements are removed.

Methyl alcohol treatment for as long as two months did not reduce B.

PRE-ARCING.

This has been recommended by many spectroscopists and is very advisable as most of the graphs of Fig. 1 show. There is an initial drop in line density during the first few minutes of arcing.

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THE PETROLOGY OF THE SILURIAN VOLCANIC SEQUENCE AT WELLINGTON, N.S.W.

By MARGARET J. COLDITZ, M.Sc.*

With five Text-figures and two Tables.

Manuscript received, August 5, 1947. Read, September 3, 1947.

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1. INTRODUCTION.

The volcanic sequence which is to be discussed in this paper lies to the north-east, east and south-east of the town of Wellington and crops out in the parishes of Micketymulga, Wellington, Bodangora and Wuuluman. The rocks are of Silurian age and form part of a volcanic belt which extends from the Jurassic sandstone near Geurie southwards through Wellington and Molong. The volcanic rocks of Orange, Cargo, Parkes, Forbes and Cobar are probably the same age.

Very little petrological work has been done on the Silurian lavas and tuffs of New South Wales and it has been tacitly assumed that they have been much altered since their formation; this study reveals that many of the low-grade minerals present in the lavas are due to deuteritic activity. It is hoped that the proof of this fact, as well as the petrological data collected, will be of value in furthering the knowledge of these rocks.

I wish to thank Dr. G. A. Joplin and Dr. W. R. Browne, of Sydney University, for the help and encouragement they have given during the preparation of this paper, and Elizabeth M. Basnett for the preparation of Figs. 2 and 3.

2. FIELD OCCURRENCE.

The outcrops between Wellington and Wuuluman consist of Silurian lavas interbedded with pyroclastic rocks and an overlying series of limestones, tuffs, breccias, slates and felsitic rhyolites. These have been named the Volcanic

* Part of this work was carried out during the tenure of Deas-Thomson Scholarships at the University of Sydney.

Series and Upper Sedimentary Series respectively (Basnett and Colditz, 1945). The whole sequence is folded into plunging anticlines and synclines from which alternating sub-meridional outcrops have been produced by erosion.

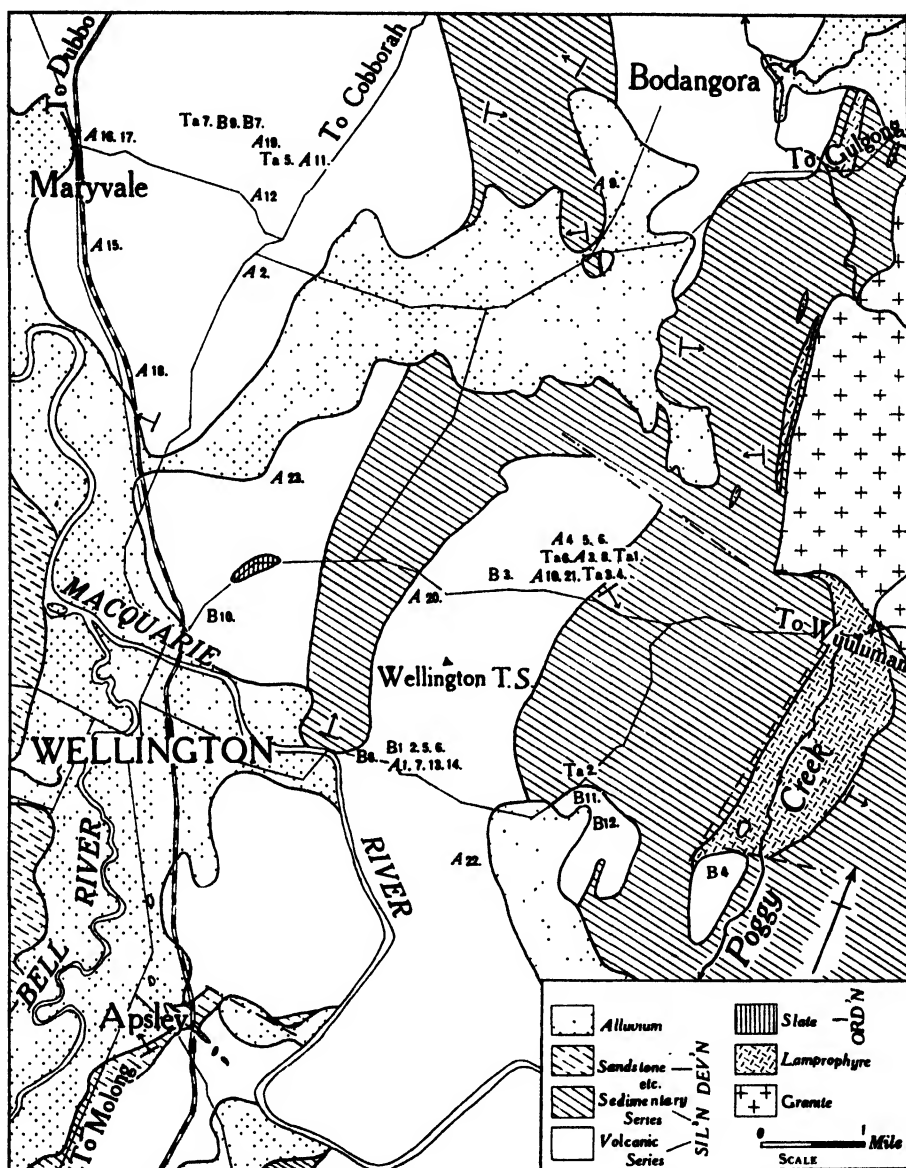


Fig. 1.—A Simplified Geological Map showing the Volcanic Series.

The Sedimentary series has been intruded by a number of sills of augite-lamprophyre (Basnett, 1942) which are believed to have a close genetic relationship to the lava flows and are included with them in the chemical discussion. The sills occur as lens-like outcrops of varying dimensions and are to be found to the east and north-east of Wellington.

The Volcanic Series can be traced beyond the confines of the map both to the north and south. Northwards the lavas are covered by the Jurassic strata at Geurie and southwards they continue towards Molong, which is 35 miles

distant. West of the Catombal Range narrow flows are found and these seem to be on the same horizon though they are more limited in thickness.

Within the series there seems to be no lava flow sufficiently continuous or distinctive to serve as a datum horizon for mapping since individual flows often merge into breccias or into xenolith-bearing flows or they may be covered with soil and alluvium. This being the case, it has so far been found impossible to examine the lava-succession over any appreciable area and collecting has been necessarily rather haphazard. However, it has been possible to examine a fairly complete sequence to the east of Maryvale in Pors. 138, 133, 182 and 123, Par. Micketymulga. It is as follows:

Glassy augite andesite (A16).

Augite andesite with albitised feldspars and vugs. Flow structure is shown by the orientation of the feldspars (A17).

Boulders from the weathering of a volcanic agglomerate.

Hornblende pyroxene trachyandesite (T7).

Porphyritic basalt (B9).

A finer phase of B9 containing rounded inclusions of the porphyritic basalt.

Porphyritic basalt (B7).

Augite andesite (A19).

Hornblende trachyandesite (T5).

Augite hornblende andesite (A11).

Volcanic agglomerate.

(The numbers used here and throughout the paper refer to Table I, which lists the type collection of slides in the museum of the Geology Department, Sydney University.)

3. LAVAS.

(i) Nomenclature.

As only three chemical analyses of the lavas have been made it has been found necessary to name and group them by petrographic methods. About 100 microscope sections have been examined, specific gravity determinations have been made and staining tests for orthoclase have been carried out (Gabriel and Cox, 1929).

The three analysed rocks are hornblende trachyandesite, augite hornblende andesite and porphyritic basalt (Table II) with silica percentages of 63, 57 and 50 and specific gravities of 2.74, 2.77 and 2.92 respectively. Petrological examination and a comparison of the specific gravities suggest that most other lavas examined are comparable with these three types, and it is assumed that they would also compare in chemical composition.

The trachyandesites and andesites are subdivided on the basis of their ferromagnesian minerals, e.g. hornblende, hornblende augite and augite andesites are found. Those rocks which contain orthoclase either in the groundmass or as phenocrysts have been named trachyandesites or trachybasalts, whilst the basalts are distinguished from the andesites by the development of an appreciable amount of augite in the groundmass, by the presence of abundant large phenocrysts of augite and by their higher specific gravities.

(ii) Petrography.

Trachyandesites.

The most acid of the trachyandesites has a sp. gr. of 2.71 and contains phenocrysts of albitic plagioclase with some orthoclase. Hornblende and augite are absent but chlorite and iron ore are developed together with much deuterio quartz and carbonates. The groundmass has a mineralogical composition similar to that of the phenocrysts.

TABLE I.

Table of Specific Gravities and Localities.

Number.	Sp. Gr.	Locality.	Name.
T1	2.71	Por. 76, Par. Nanima.	Trachyandesite.
T2	—	Por. 86, Par. Nanima.	Trachyandesite.
T3	2.74	Por. 94/122, Par. Nanima.	Hornblende trachyandesite. (Analysed.)
T4	2.75	Por. 94, Par. Nanima.	Hornblende trachyandesite.
T5	2.77	Por. 123, Par. Micketymulga.	Hornblende trachyandesite.
T6	2.75	Por. 94, Par. Nanima.	Hornblende trachyandesite.
T7	2.87	Por. 182, Par. Micketymulga.	Hornblende augite trachyandesite.
A1	2.76	Por. 31, Par. Nanima.	Hornblende andesite.
A2	—	Por. 1, Par. Nanima.	Hornblende andesite.
A3	—	Por. 94, Par. Nanima.	Hornblende andesite.
A4	—	Por. 94, Par. Nanima.	Hornblende andesite.
A5	—	Por. 94, Par. Nanima.	Hornblende andesite.
A6	—	Por. 94, Par. Nanima.	Hornblende andesite.
A7	—	Por. 31, Par. Nanima.	Hornblende andesite.
A8	2.76	Por. 94, Par. Nanima.	Hornblende andesite.
A9	—	Bodangora Common.	Hornblende andesite.
A10	—	Por. 94/122, Par. Nanima.	Hornblende andesite (in breccia).
A10a	—	Por. 31, Par. Nanima.	Altered hornblende andesite.
A11	2.75	Por. 123, Par. Micketymulga.	Augite hornblende andesite.
A12	2.77	Por. 251, Par. Micketymulga.	Augite hornblende andesite. (Analysed.)
A13	2.80	Por. 31, Par. Nanima.	Augite hornblende andesite.
A14	2.88	Por. 31, Par. Nanima.	Augite hornblende andesite.
A15	—	Por. 73, Par. Micketymulga.	Augite hornblende andesite.
A16	2.81	Por. 133, Par. Micketymulga.	Glassy augite andesite.
A17	2.84	Por. 138, Par. Micketymulga.	Augite andesite.
A18	2.87	Por. 74, Par. Micketymulga.	Augite andesite.
A19	2.92	Por. 123, Par. Micketymulga.	Augite andesite.
A20	—	Por. 23, Par. Nanima.	Augite andesite.
A21	—	Por. 94, Par. Nanima.	Augite andesite.
A22	—	Por. 51, Par. Nanima.	Glassy augite andesite.
A23	2.91	Por. 1, Par. Nanima.	Glassy augite andesite.
B1	—	Por. 31, Par. Nanima.	Basalt.
B2	2.82	Por. 31, Par. Nanima.	Porphyritic basalt.
B3	2.92	Por. 93, Par. Nanima.	Porphyritic basalt. (Analysed.)
B4	2.97	Por. 50, Par. Nanima.	Porphyritic basalt.
B5	2.97	Por. 31, Par. Nanima.	Porphyritic basalt.
B6	—	Por. 31, Par. Nanima.	Porphyritic basalt.
B7	2.99	Por. 182, Par. Micketymulga.	Porphyritic basalt.
B8	3.00	Por. 31, Par. Nanima.	Porphyritic basalt.
B9	3.02	Por. 182, Par. Micketymulga.	Porphyritic basalt.
B10	—	Near Golf Links.	Porphyritic basalt.
B11	2.83	Por. 49, Par. Nanima.	Porphyritic trachybasalt.
B12	2.92	Por. 49, Par. Nanima.	Porphyritic trachybasalt.

The hornblende trachyandesites are the most commonly developed of this group of lavas and one of these has been analysed (Table 2). The most basic type sectioned contains orthoclase in the groundmass and not as phenocrysts and has a sp. gr. of 2.87. This high density is probably due to the fact that hornblende is almost completely resorbed to iron ore.

In hand specimen the trachyandesites are grey, aphanitic rocks with macroscopic phenocrysts of glassy or cream-coloured felspar and black ferro-magnesian minerals. These phenocrysts may show parallelism in their arrange-

ment and deuteric alteration is indicated by the presence of light patches and irregular veins in the rock.

Thin sections reveal that the groundmass consists of tiny felspar laths which show trachytic fabric and are associated with abundant granules of iron ore as well as epidote, occasional sphene and perhaps some needles of hornblende or pyroxene. A green to greyish granular material may be residual glass. Veins of epidote, calcite and albite sometimes occur in the more altered varieties.

The felspar phenocrysts are idiomorphic to subidiomorphic and are tabular to prismatic in habit. They are as much as 3 mm. in length and when the composition can be determined it is albitic, becoming more calcic in the varieties which approach the andesites in composition. In these types it tends towards oligoclase and may even be andesine. Extensive alteration often masks the composition of the felspar, the secondary minerals being albite, sericite, epidote, chlorite and some kaolin.

Hornblende is found as idiomorphic to subidiomorphic phenocrysts which have been rounded by corrosion and which usually show some alteration to epidote, chlorite, sphene, iron ore and carbonates. The size of the phenocrysts is variable, often reaching 3 mm., although the average length is less than 1 mm. They are brownish-green in colour; the pleochroism ranges through pale yellow, greenish brown and bluish-green and the extinction angle is 15° to 19° . An exception to this is found in T5 where all the phenocrysts are of brown hornblende associated with smaller phenocrysts of apatite.

The augite in T7 is fine-grained and idiomorphic to subidiomorphic. It is pale grey in colour, has an extinction angle of 46° and shows slight corrosion. Inclusions of iron ore and felspar are present.

Andesites.

The andesitic group of lavas is distinguished from the trachyandesites by the absence of orthoclase and from the basalts and trachybasalts by the absence of augite in the groundmass. Their specific gravities range from 2.76 to 2.92, the average being about 2.83, whilst the felspar compositions vary from andesine to labradorite. An augite hornblende andesite has been analysed (Table 2).

Hornblende Andesites. Without applying staining tests for orthoclase it is difficult to distinguish hornblende andesites from hornblende trachyandesites. The former are dark grey to greenish-grey rocks with cream or white felspar phenocrysts associated with hornblende crystals.

In thin section the groundmass is grey and translucent with dark patches which produce a mottled appearance. Tiny felspar laths show a tendency towards trachytic fabric and are associated with granules of sphene, epidote, chlorite, ilmenite and idiomorphic crystals of apatite. Veins and vughs of epidote, calcite and chlorite occur frequently and have produced much alteration in the rocks.

The composition of the felspar varies from albite-oligoclase to andesine-oligoclase though alteration usually gives the felspar crystals a greyish and speckled appearance. The alteration products are kaolin and sericite with occasional epidote and chlorite and they are often arranged zonally. In A3 the felspar crystals consist of a core of epidote and clinozoisite sometimes with chlorite, surrounded by a clear margin of felspar which is probably oligoclase.

The hornblende shows prismatic habit and in A3 is as much as 3 mm. in length. It is brownish-green in colour, has an extinction angle of 19° and is strongly pleochroic (greenish-yellow, brownish-yellow and grass green). Many crystals are corroded and some have released iron ore around the margins and as inclusions. Alteration is fairly well advanced, the products being epidote, chlorite and sphene as well as carbonates and ilmenite. In some rocks the

hornblende has been entirely replaced by these minerals and can be recognised only by its habit.

Augite Andesites. The augite andesites are characterised by the presence of variable amounts of glass at different stages of devitrification. A16, a pitchy black rock with felspar phenocrysts, has the most glass and also the lowest specific gravity of the augite andesites which have been examined. The others are greenish-grey in colour with tabular felspars which usually show signs of albitisation.

In thin section the groundmass is translucent to almost opaque and is brown to dirty grey in colour. Under crossed nicols microlites of felspar are sometimes visible in a matrix which shows slight double refraction. Under higher magnification this material has a rough bleb-like appearance and shows slight double refraction or it consists of pale green isotropic granules associated with tiny granules of iron ore and chloritic material. The material is thought to be due to the devitrification of a glassy matrix in the original lava.

The felspar phenocrysts are very abundant and are usually altered but in A16 they are comparatively fresh andesine. These crystals are clear and corroded and show pseudo-inclusions. Zoning is developed, the zones showing an increasing refractive index; some have the composition $Ab_{55}An_{45}$. In A17 the felspar seems to have been more basic than this and may have approached labradorite but both here and in other rocks it has been altered to sericite, kaolin and chlorite.

The augite is pale green in colour and much fresher than the felspar. It shows some corrosion and in A16 and A17 contains fine Schiller inclusions. Chloritisation has occurred, occasionally producing complete pseudomorphs. Some pseudomorphs consist of epidote, chlorite, serpentine and sphene and are intergrown with the augite. They show an octagonal cross section and may have been hypersthene. In A18 pseudomorphs of granular quartz, serpentine or chlorite, carbonates and talc assume a regular form like that of olivine.

Augite Hornblende Andesites. Intermediate between the hornblende and augite andesites are types which contain both of these ferromagnesian minerals in variable proportions. The hornblende is brownish-green when unaltered and usually of larger grain size than the augite. In one rock it reaches 5 mm. in length while in the same rock augite is no longer than 1 mm. Corrosion has caused rounding of the phenocrysts and deposition of iron ore in the hornblende. Felspar phenocrysts have been altered to kaolin, sericite, epidote and albite.

Basalts and Trachybasalts. The basalts are characterised by the presence of large phenocrysts of augite set in a groundmass which contains granular augite. Felspar phenocrysts may, or may not be present. The specific gravities vary from 2.82 to 3.02 and the felspar composition, where determinable, is labradorite. In the case of the trachybasalts orthoclase is present in the felspar of the groundmass.

The basalts are greenish-grey, dark grey or purple in colour, according to the amount of and to the type of deuteric alteration in the rock; in nearly every case vugs filled with green, pink or white minerals are present. Large tabular crystals of pyroxene are visible and sometimes there are creamy coloured felspars as well.

In thin section the groundmass is brownish and speckled unevenly with iron ore. It consists of felspar laths with interstitial augite, carbonates, chlorite, iron ore and sphene. Epidote is present in some rocks, as is also interstitial glass. Patches of deuteric minerals are very common.

The felspar phenocrysts are idiomorphic to subidiomorphic and of tabular habit. They are rarely fresh, being altered to kaolin, sericite, chlorite, carbonates and sometimes albite. These products may be zonally arranged or may preserve,

by their orientation or distribution, the original cleavage or twinning of the crystal. In B7 a felspar crystal has been completely pseudomorphed by carbonates and chalcedony with some chlorite, the minerals being arranged in bands in a regular structure (Fig. 3H). In another basalt red and green patches in the rock seem to be due to pseudomorphs of felspar by haematite and carbonates.

The augite phenocrysts show a tendency to be glomero-porphyritic. They are light grey in colour; are idiomorphic to subidiomorphic and in B7 are as much as 4 mm. across. Colour zoning and polysynthetic twinning are developed and corrosion has caused the rounding of crystal margins and the development of pseudo-inclusions. Slight alteration to chlorite, carbonates and iron ore has occurred.

Vughs or solution cavities are numerous and contain chlorite, carbonates, epidote, zeolites and chalcedony. They vary in diameter from about 10 cm. to <2 mm. and usually show a zonal arrangement of minerals (Fig. 3).

The flow which has been called a trachybasalt has been examined in two phases in slides B11 and B12. The groundmass consists of laths of felspar and purplish augite with granules of iron ore, epidote, sphene as well as interstitial chlorite and carbonates. The presence of orthoclase in the groundmass felspar has been verified by staining tests.

The rock is grey and is set with greenish tabular felspars as much as 10 mm. in length (B11) and augite crystals which are more than 6 mm. (B12). B12 is the coarser phase of the flow and the groundmass tends to be doleritic.

The felspar phenocrysts have been zonally altered to sericite with some albite, epidote and carbonates.

(iii) Occurrence of Xenoliths.

Inclusions are plentiful in many of the lava flows, often to such an extent that the flow may be mistaken for a breccia especially when weathering is advanced. A noteworthy feature of most of these inclusions is that even though they differ from the enclosing rock in grainsize they have a similar mineralogical composition. Their contours are rounded suggesting a certain amount of resorption which gives them the appearance of water-worn boulders.

Several xenoliths have been examined in thin section and in every case they possess much coarser grainsize than the enveloping rock and are clearly defined from it. They consist of stout, interlocking felspar crystals, sometimes with plates and crystals of hornblende or augite and always with interstitial chlorite, epidote, iron ore and carbonates (Fig. 2B).

A xenolith in an augite hornblende andesite consists of large plates of green hornblende with large apatite prisms, small crystals of augite and felspar, and epidote, chlorite and carbonates with a little iron ore in the interspaces.

The crystals present in the xenoliths are usually similar in composition to the phenocrysts of the enclosing lava but this is not always so as in one of the hornblende trachyandesites a xenolith contains some augite. The xenoliths vary in size from 5 mm. by 2 mm. to several centimetres in diameter.

A. G. Macgregor (1938) has recorded from the modern volcanic region of Montserrat xenolith-bearing lavas which resemble these in habit and crystallinity. He suggests that they are "partly crystallised magma that once lined the walls of the magma conduit. During renewal of upward movement of similar magma, pieces of semi-crystallised wall rock were torn from the conduit sides, and incorporated as xenoliths in the ascending magma". The coarse grainsize and interstitial filling of deuteric material certainly suggest that the crystals were formed slowly. The interspaces may have been filled with residual material either before or after extrusion.

The incorporation of inclusions of lava, slate, dolerite, etc., as well as the cognate xenoliths in the lavas at Wellington, may be due to explosive activity preceding eruption and to the addition of talus material after extrusion.

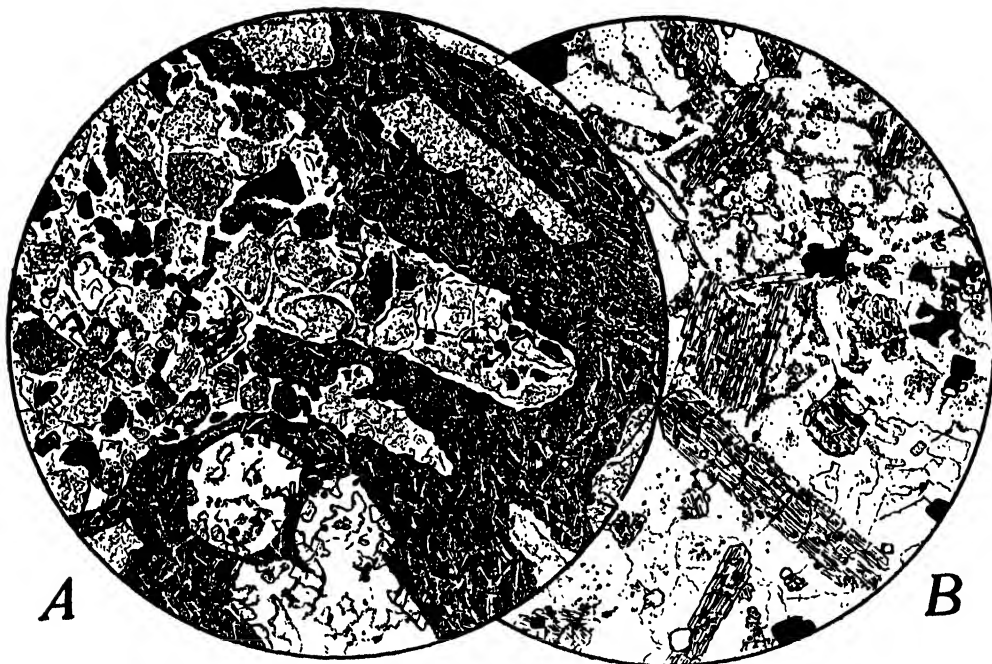


Fig. 2.

- A. A lava fragment (probably porphyritic trachybasalt) included in a tuff. The tuff shows an intrusive relationship towards the lava and consists of fragments of lava and altered primary minerals which now consist of carbonates, sericite and chlorite, set in a fine cement of the same materials. Deuteric alteration has also affected the dark coloured lava in which iron ore has been released and feldspars completely sericitised. Intrusion is apparently effected by the action of deuteric vapours. $\times 20$.
- B. Xenolith included in porphyritic hornblende andesite. The andesite has phenocrysts of hornblende and plagioclase set in a fine felspathic groundmass and the xenolith consists of feldspar and hornblende in interlocking crystals of fairly even grain size. Deuteric activity has affected both lava and xenolith altering hornblende to chlorite, epidote and carbonates and causing sericitisation of feldspar. $\times 20$.

4. PYROCLASTIC ROCKS.

(i) Nomenclature.

The pyroclastic rocks include extremely fine-grained tuffs, breccias and agglomerates which are formed of angular and rounded blocks measuring as much as 3 ft. by 3 ft. 6 ins. in cross section. They may be divided broadly into two groups :

Lithic tuffs, breccias and agglomerates, and
Crystal tuffs.

The former are composed mainly of lava fragments and are found interbedded with the lavas, while the crystal tuffs occur for the most part with the slates and limestones of the Upper Sedimentary series (Basnett and Colditz, 1945). The breccias which contain both lava and other fragments occur near the top of the Volcanic series.

(ii) Petrography.***Lithic Tuffs.***

In many of the lithic tuffs and breccias fragments of lavas are massed together so closely that a tuffaceous matrix is not always visible in hand specimen. Such a rock occurs in Pors. 203/101, Par. Nanima; it consists of small angular rock fragments about $\frac{1}{2}$ inch across and coloured pale green, bluish green, purple or almost black. A few small cavities filled with carbonates are present. Examination of a thin section reveals that the dark fragments have a great concentration of iron ore and that some are welded by a narrow vein of felsitic material (possibly chalcedony) whilst others are joined by tuffaceous material or are in direct contact. The tuffaceous material consists of crystal fragments of greenish-brown hornblende, colourless augite and feldspar and numerous tiny pieces of rock cemented with felsitic material. Chlorite is abundant and some carbonates are present. Where the tuff adjoins a fragment of lava there is sometimes evidence of mechanical stoping (Fig. 2A).

Other tuffs and breccias appear more homogeneous as there is less colour variation. One type cropping out in Por. 182, Par. Micketymulga is a grey aphanitic rock resembling a lava; actually it consists of fragmental feldspar, augite and hornblende crystals together with many small pieces of lava which vary in crystallinity, some being glassy and others hyalopilitic; some fragments have been impregnated with iron ore; chlorite is abundant.

The presence of rock types foreign to the lavas of the Volcanic series is not noticeable in the finer-grained rocks and it is possible that they do not occur, but in some of the coarser breccias there are pebbles of quartz dolerite, slate and other rock types. The pebbles are either rounded or angular and are as much as 3 or 4 inches in diameter.

Crystal Tuffs.

The crystal tuffs overlie the lavas for the most part and are variable in grain size. In hand specimen the fine-grained types show sub-conchoidal fracture and are medium to dark grey aphanitic or cherty rocks. Some recrystallised types are buff coloured and mottled and these may contain small rounded quartz crystals. The coarser types contain macroscopic feldspar laths in a fine groundmass.

Thin sections of the fine tuffs reveal a porphyritic grain size with small phenocrysts (up to 0.5 mm.) of albite-oligoclase and quartz embedded in a very fine-grained groundmass of similar material. A brownish, green or grey material is patchily distributed and seems to consist of chlorite, epidote and iron ore. Carbonates and micaceous material are sometimes developed.

Most of these tuffs appear to have been recrystallised as in some sections both the phenocrysts and groundmass minerals show distinctly crenulated margins. In a tuff from Por. 1, Par. Nanima, sieve-like plates of hornblende have been formed.

The coarser crystal tuffs consist of interlocking feldspar laths up to 3 mm. in length. Small quartz crystals are present as well as fibrous chlorite and epidote. The feldspars are mainly albitic but some orthoclase and oligoclase may occur.

The presence of chlorite to the exclusion of hornblende and pyroxene is an interesting feature of most of the crystal tuffs.

5. ALTERATION.

One of the most interesting facts arising from an examination of the volcanic rocks at Wellington is that almost without exception, they have suffered some degree of alteration. The presence of veins and vugs within the rocks as well

as the nature of many of the mineralogical changes make it fairly clear that most of the alteration has been caused by deuteric activity during the period of vulcanism rather than by post-Silurian processes of weathering and metamorphism. The devitrification of the glassy groundmass of some of the augite andesites may be due either to deuteric action or to slight regional metamorphism.

Most of the lavas, particularly the basalts, in which the mineral constituents have been intensely altered, show veins and vughs filled with deuteric minerals. The veins are often visible in hand specimen and vughs up to 6 inches across are seen more rarely but there is ample microscopic evidence of both. The deuteric minerals are albite, epidote, calcite, chlorite, chalcedony and zeolites and these are usually arranged zonally in the cavities. The lining of the cavity is usually of chlorite and chalcedony or more rarely epidote (Fig. 3D) the centre being filled with calcite, chlorite or zeolites. Although not identical with the deuteric filling of the vesicular cavities in the trachybasalt at Port Kembla (Browne and White, 1928) these minerals are quite similar in composition and arrangement.

Another noticeable effect of deuteric activity, and one readily noticed in hand specimen, is the change in colour of the lavas. The less altered types are grey to dark grey in colour but alteration has produced greenish-grey, bluish-grey, blue and purple rocks. The latter colour occurs frequently and is due to a strong introduction of iron by magmatic solutions. Comparable changes in colour due to deuteric activity have been recorded in lavas at Blair Duguid (Browne and White, 1926) and Port Kembla (Browne and White, 1928). A fact which restricts these colour changes to the time of extrusion is that fragments of multi-coloured lavas are preserved in the lithic tuffs and breccias which are interbedded with the flows. The breccias themselves sometimes contain cavities filled with carbonates, chlorite and chalcedony but any alteration produced in the fragments after deposition of the breccia is superimposed upon a stronger and earlier alteration in the fragments.

The original mineral constituents of the lavas have suffered a considerable amount of alteration, especially the feldspar phenocrysts, which are never found absolutely unaltered and are often completely pseudomorphed even though the groundmass feldspar may have been but slightly changed. Hornblende, too, is much altered, while augite often remains quite fresh. In general, the groundmass is less altered than the phenocrysts even though the products of alteration are similar.

The alteration products of the feldspars are often arranged in zones or they may preserve some other mineral structure such as cleavage or twinning. They consist of albite, sericite, epidote, chlorite, carbonates and kaolin; of these albite is found most frequently as the replacing mineral in the trachyandesites while in the basalts mica and carbonates are strongly developed. The chemical analyses show an increase in the proportion of K_2O to Na_2O in the basaltic type and this is probably due to the presence of sericite. In one porphyritic basalt the feldspar has been completely pseudomorphed by haematite and carbonates.

The most noticeable change in the hornblende phenocrysts is the development of fine granules of iron ore around the borders of the crystals. This process is sometimes sufficiently advanced to produce complete pseudomorphs and is due to resorption rather than to deuteric action. Macgregor has recorded similar resorption of hornblende in the lavas at Montserrat (1938). Some deuteric alteration occurs along cleavage and cracks in the crystal forming epidote, chlorite, sphene, iron ore and carbonates.

Chloritisation of augite sometimes occurs and in the basalts carbonates and iron ore also occur as alteration products. The relative freshness of augite in otherwise much altered rocks has been recorded from Maitland (Browne,

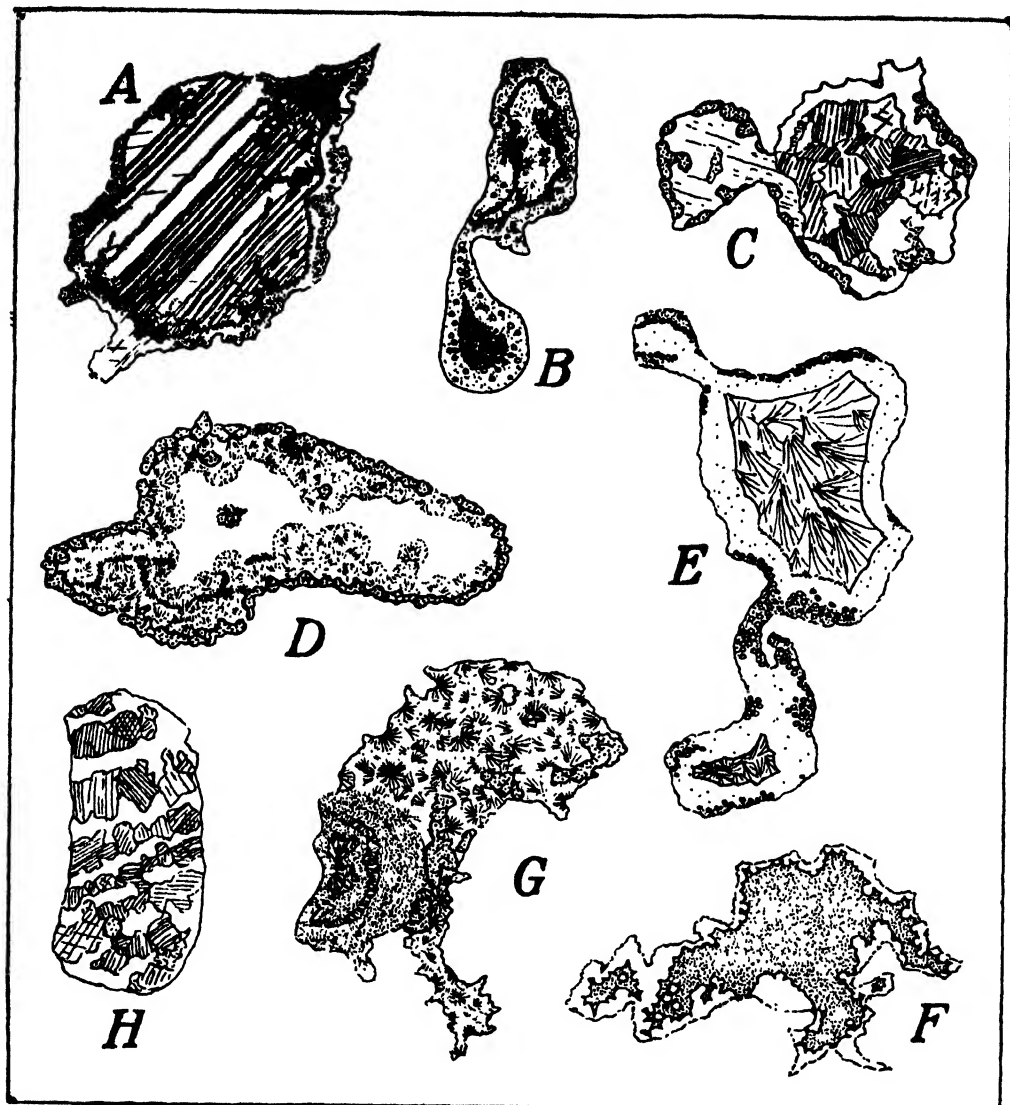


Fig. 3. Evidences of Deuteritic Activity in the Lavas. $\times 16$.

- A. Slide A22. This vugh has a discontinuous lining of pale green chlorite followed by a narrow zone of carbonates, both minerals containing globules of chalcedony. Next comes an irregular layer of fibrous blue-green chlorite and the centre is filled with carbonates.
- B. Slide A22. This cavity is almost completely filled with chlorite. The lining is pale green and almost isotropic with globules of chalcedony. Within this is a narrow zone of larger bluish-green fibrous crystals while the central portion contains a paler fibrous chlorite.
- C. Slide B8. A few grains of epidote and an occasional patch of chlorite form the outer layer of this vugh, which is followed by a discontinuous zone of chalcedony and an infilling of carbonate.
- D. Slide B8. Epidote is developed here as an almost continuous outer layer, followed by a wide irregular zone of pale green fibrous chlorite and a centre of chalcedony.
- E. Slide A10a. Chlorite with chalcedony globules is sparsely developed around the walls of the vugh and the interior consists of fine fibrous zeolite bounding a central region with coarser crystals.
- F. Slide B7. The walls of this cavity are lined with chalcedony, which shows a botryoidal surface against the infilling chlorite.
- G. Slide B1. Pale green fibrous chlorite with a few grains of epidote compose the greater part of this vugh, but in the lower portion of the diagram layers of chalcedony and chlorite are zonally arranged.
- H. Slide B7. The pseudomorph of a feldspar crystal in which granular carbonates and chalcedony

1922) and from Prospect (Browne, 1924). In the analcite dolerite at Prospect the only alteration is to chlorite with occasional calcite as is found at Wellington.

In the vicinity of the Bodangora gold mines and to the south-west of Apsley railway station the rocks have been intensely altered either by deuteric action, by quartz veins from the Wuuluman granite, or by both. At the former locality the thin section of an andesite shows almost complete obliteration of previous rock structures as alteration to carbonates and mica is practically complete. There is some chlorite and kaolin and a few granules of feldspar remain in the ghosts of former feldspar phenocrysts. Near Apsley there is evidence of strong introduction of iron ore by deuteric solutions; it forms a dense deposit in granules around vugs and cracks in the rock. Another flow which is from Por. 267, Par. Wellington, and is an altered porphyritic basalt has its augite phenocrysts partly replaced by quartz and copper while the remainder of the rock has been pseudomorphed by epidote and quartz.

About $2\frac{1}{2}$ miles south-west of Bodangora a few lava flows come into contact with the Wuuluman granite. In these the groundmass has been completely recrystallised to feldspar granules and fibrous green hornblende which is arranged in parallel groups. The feldspar phenocrysts show partial recrystallisation around the edges and the inclusions have formed tiny fibres of green hornblende.

6. PETROGENESIS.

(i) Chemical Discussion.

It is not a simple matter to interpret the petrology of this group of lavas, as no definite sequence of extrusion has been observed over a large area. This fact is not surprising when one considers the complexity of present-day volcanic regions where there is much overlapping of flows from different vents, where lavas merge into agglomerates and where a great deal of contemporaneous erosion and earth movement takes place. The Wellington lavas must have been laid down under conditions similar to these and they have been faulted and folded since their deposition.

Three volcanic rocks and three hypabyssal types have been analysed covering a range of 17% SiO_2 (Table II). The analysed lavas have a range of 12% SiO_2 and as they are fairly normal types of trachyandesite, andesite and basalt this should approach the complete silica range of the Wellington lavas.

The analysis of the porphyritic basalt shows a near relationship to "hessose" of the C.I.P.W. classification, augite hornblende andesite resembles "andose" and hornblende trachyandesite is comparable with "pulsakose".

In the norms of the three lavas (Table IIA) there is a noticeable increase in normative orthoclase in the trachyandesite and the plagioclase feldspar shows a pronounced increase in the proportion of albite to anorthite.

Mineralogically the basalts appear to be of the tholeiitic magma of Kennedy (1933), since they contain pyroxene to the exclusion of olivine. Chemically, however, the analyses are not similar to his except in the silica percentage: also the line of descent for the tholeiitic magma (viz. tholeiitic basalt \rightarrow andesite \rightarrow rhyolite) is contradicted at Wellington by the presence of the trachyandesites which Kennedy places in the olivine basalt sequence.

The group of lamprophyre sills to the north-east of Wellington appear to be related to the lava series as they show close affinities to them both in appearance and in field occurrence (Basnett, 1942; Basnett and Colditz, 1945). Analyses of three of them, together with the three lavas, have been plotted on a variation diagram which is figured below (Fig. 4). These rocks have been referred to as augite lamprophyres throughout the text but are listed as amphibolites in Table II. This is due to the fact that the augite has in most cases been altered to amphibole by contact metamorphism, a change which is obvious only in thin section.

Since analyses are so few and as there have been deuteric changes in the lavas the chemical relations must be somewhat conjectural, but despite this the diagram has some features of interest.

A specific gravity curve has been superimposed and shows a good deal of conformity with the amount of lime and magnesia present in the rocks.

TABLE II.

Table of Analyses.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO ₂	45.49	47.52	49.24	50.46	56.65	62.55	50.85	50.71
Al ₂ O ₃	10.49	12.50	13.85	17.99	20.37	17.46	16.07	17.92
Fe ₂ O ₃	6.44	1.08	4.88	1.06	1.24	2.37	4.58	5.14
FeO	4.36	6.26	6.55	5.76	3.28	2.03	6.45	4.73
MgO	18.48	16.50	8.34	6.78	3.20	1.43	4.23	4.67
CaO	10.72	13.07	10.94	10.91	4.31	2.55	7.83	7.28
Na ₂ O	0.89	0.46	2.55	0.97	5.65	4.99	2.57	2.49
K ₂ O	1.25	0.92	1.32	1.63	2.75	4.78	2.03	2.16
H ₂ O+	1.55	0.85	0.72	2.38	1.43	0.85	2.41	1.96
H ₂ O-	0.11	—	0.16	0.04	0.11	0.08	0.16	0.62
TiO ₂	0.36	0.67	0.62	0.88	0.67	0.52	1.30	1.04
P ₂ O ₅	0.24	tr.	0.31	0.29	0.29	tr.	0.33	0.35
MnO	0.15	0.14	0.17	0.12	0.08	0.44	0.09	0.09
CO ₂	—	—	—	1.12	—	—	0.79	0.48
Total	100.53	99.97	99.65	100.39	100.03	100.05	99.69	99.64
Sp. Gr.	3.10	3.13	3.09	2.92	2.77	2.74	2.92	2.80

I. Spinel Amphibolite. Por. 14, Par. Bodangora. Anal. E. M. Basnett.

II. Epidote Amphibolite. Por. 83, Par. Bodangora. Anal. M. J. Colditz.

III. Felspar-bearing Amphibolite. Wuuluman Road Crossing of Poggy Creek. Anal. E. M. Basnett.

IV. Porphyritic Basalt. Por. 93, Par. Nanima. Anal. M. J. Colditz.

V. Augite Hornblende Andesite. Por. 251, Par. Micketymulga. Anal. M. J. Colditz.

VI. Hornblende Trachyandesite. Por. 94, Par. Nanima. Anal. M. J. Colditz.

VII. Augite Porphyrite. Por. 145, Par. Copper Hill, Molong. Anal. R. Brewer.

VIII. Augite Andesite. Por. 1, Par. Bell, Molong. Anal. D. Moye.

TABLE IIA.

Norms.

	IV.	V.	VI.
Quartz	6.36	—	7.32
Orthoclase	9.45	16.68	28.36
Albite	8.38	48.21	42.44
Anorthite	39.75	19.74	11.12
Corundum	—	0.71	—
Diopside	4.48	—	1.33
Hypersthene	23.19	2.39	3.89
Olivine	—	6.93	—
Magnetite	1.86	1.86	3.48
Ilmenite	1.67	1.37	0.91
Apatite	0.67	0.67	—

At the basic end of the series magnesia is dominant and is associated with high lime and iron, a moderate amount of alumina and low alkalis. This composition is expressed mineralogically by the dominance of augite (altered to amphibole) in the most basic rocks where felspar is rare. With increasing

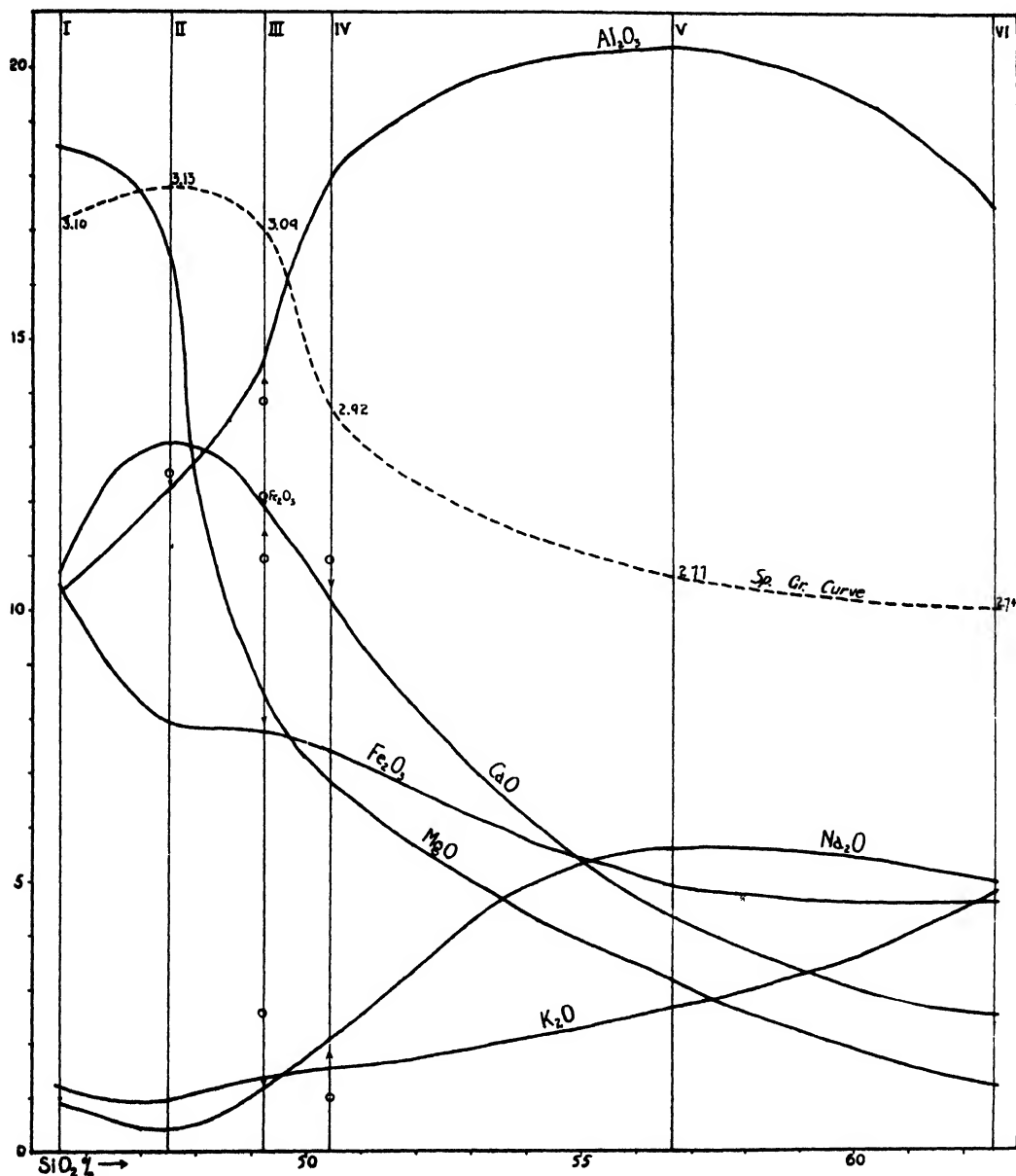


Fig. 4. A Variation Diagram of the Lava Series and Lamprophyres.
For analyses and names of rocks, see Table II.

silica plagioclase becomes more abundant and the increase in lime involved in its formation is shown by the steep rise in this curve between analyses 1 and 2; this is accompanied by a rise in alumina and a fall in magnesia and iron.

The lavas are joined by more gentle curves which show decreasing lime, magnesia and iron and increasing alkalis. With the formation of anorthite the

alumina curve rises, but as the plagioclase becomes albitic and hornblende develops the soda and alumina curves reach a maximum and then fall towards hornblende trachyandesite.

The potash in the basalt is probably contained in the sericite alteration product of the plagioclase. There is a very pronounced increase in soda in the augite hornblende andesite due to an increase in the proportion of albite in the plagioclase and perhaps also to more albitisation of the felspar. In the trachyandesite the development of orthoclase is indicated by a rise in the potash curve and a very slight fall in soda. In these rock types the process of albitisation is more important than that of sericitisation.

The variation diagram and specific gravity curve indicate that the lavas and lamprophyres form a volcanic suite in which an increase in silica percentage involves a decrease in specific gravity and an increase in the albite molecule of the felspar.

A graph in which the silica percentages of the lavas have been plotted against their specific gravities suggests the range of silica for the rock types. On this diagram an average of the three analysed amphibolites has been used to represent the lamprophyres. The range of specific gravities of the lavas has been obtained from Table I and exceptional values have not been considered as they are probably due to excessive alteration. The silica percentages of the lamprophyres are seen to vary from 45 to 49, the basalts from 49 to 50.5, the andesites from 50.5 to 58, and the trachyandesites have more than 56.5% SiO_2 .

(ii) Magmatic History.

A comparison of the mineralogy of the Wellington lavas and lamprophyres as well as a study of their analyses suggests that the differences in composition of lavas and sills can most easily be accounted for by the sinking of crystals in a magma reservoir as formulated by Bowen (1928).

The original composition of the magma in the reservoir was probably andesitic and intermediate between analyses IV and V (*vide* Table II and Fig. 5), with a silica percentage of about 54. In discussing the origin of the Garabal Hill-Glen Fyne complex and also the volcanic rocks of Lower Old Red Sandstone age (Nockolds, 1941), is of the opinion that the parent magma had the composition of a pyroxene-mica diorite or a pyroxene andesite. The analyses which he gives are intermediate in composition between the augite hornblende andesite and the porphyritic basalt at Wellington. This magma, then, must have been very like that which produced the volcanic sequence at Wellington.

The crystallisation of augite and felspar was followed by the extrusion of augite andesites and porphyritic basalts. A period of quiescence was accompanied by sinking of the augite due to its high density and subsequent formation of hornblende. This allowed for the extrusion of hornblendic types as well as lavas containing both hornblende and augite.

The presence of microphenocrysts of apatite in the hornblende andesites, as well as very abundant alkalis, bears out the idea that this lava type may have formed one of the upper layers in the magma reservoir together with the trachyandesites.

With a fresh influx of material or a mixing of the residual magma a repetition of the process would occur, except that in the latter case more basic types would be formed.

Bowen's theory could also explain the occurrence of augite andesites and porphyritic basalts with different proportions of augite and felspar phenocrysts, since in the zone where augite was most abundant felspar would be least abundant. The augite lamprophyre is the extreme case where no felspar phenocrysts are present and the residual magma with its large crowded augite

crystals was intruded as lenses in the soft sediments at the close of, or during, Silurian time.

During the earlier stages of volcanic activity lavas were poured out and intermittent explosive action caused the formation of beds of pyroclastic material. The centres of eruption were situated close to the sea and lenses of limestone were formed when conditions remained stable for a sufficiently long period. At the close of the period of vulcanism explosive action increased in frequency as indicated by an increase in breccias, tuffs and agglomerates; these were succeeded in more peaceful times by tuffaceous sediments in which the tuff may have been derived from distant sources.

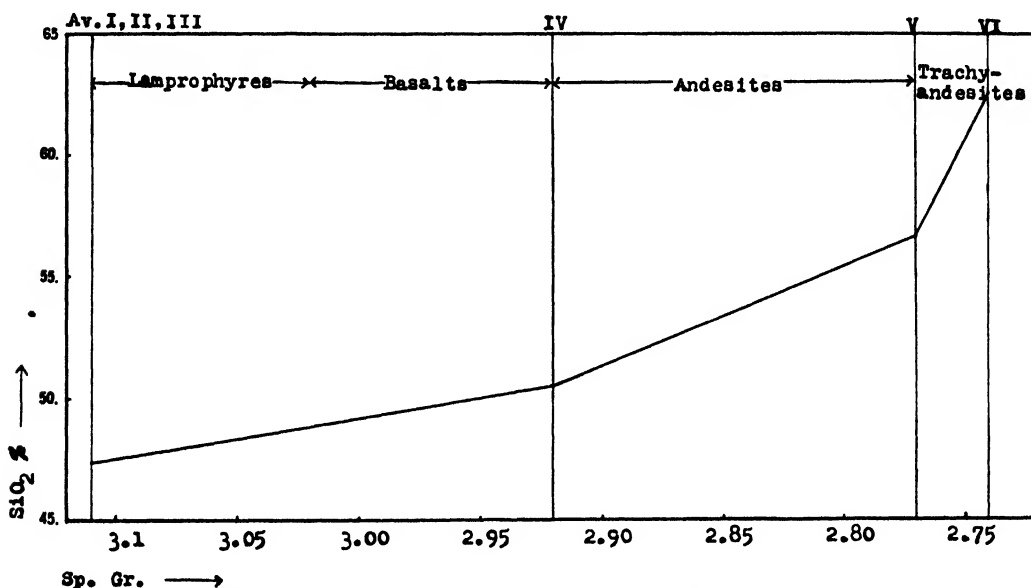


Fig. 5. Diagram showing the Range of Silica Percentages and Specific Gravities.

The lavas were probably extruded from several different vents as the flows are not persistent over any great area but all show certain phenomena in common such as deuteric alteration and xenoliths. The flows were all porphyritic but varied in the amount of glass present, some having an entirely glassy matrix and others being quite free from glass. Many hornblendic types had their phenocrysts resorbed due to decrease of temperature and pressure during ejection and were left with "ghost" phenocrysts of iron ore. Magma often began to crystallise within the vent but when eruption took place the crystals were torn from the walls and included as cognate xenoliths in the lava. Other xenoliths, mainly of lava, would be gathered up from talus material lying in the path of the flow.

In some cases deuteric alteration probably commenced while the lava was still pouring from the vent and continued until the flow was quite cool. The remaining volatiles became segregated in the vesicles near the surface of the flow and crystallised there.

Intermittent explosive action produced fragmentation of the lavas and their phenocrysts and sometimes included rocks foreign to the area; this was especially so when explosive activity was dominant.

7. COMPARISON WITH OTHER AREAS.

The volcanic rocks of the Wellington district can be traced southwards to Molong, where they have been examined by R. Brewer, B.Sc., and D. Moye,

B.Sc. Two analyses from Molong have been included in Table II. The extent of the lavas, from the Jurassic rocks near Geurie, southwards through Wellington and Molong to the Orange district, is a distance of about 70 miles.

At Cargo, to the south-west of Orange, Andrews has recorded andesites, trachytes, dolerites and pitchstones, interbedded with breccias and tuffs and associated with Silurian sediments (1915). He also describes (1910) augite andesites banded with slates and tuffs in the Forbes-Parkes district which lies to the south-west of Wellington.

To the south-east of Orange, augite andesites similar to those at Wellington have been described by Whitworth at Blayney (1938) and Harper (1920) recorded both augite andesite and serpentine from Lucknow. The latter occurs in lenses and is intrusive; its correlation with the augite lamprophyre is quite possible.

These Silurian volcanic rocks, many of which are auriferous, show petrographical affinities to one another and form part of a petrographical province which occupied the central part of the state during the Silurian period (Browne, 1929). That it had rather alkaline affinities is supported by the fact that there are moderately high alkalis in the analysed rocks from Wellington and Molong (Table II).

The complex nature of the Wellington lavas with their overlapping xenolithic flows, resorbed hornblende crystals and interbedded tuffs and limestones is not unlike the volcanic island of Montserrat, where recently formed lavas show similar characteristics.

8. SUMMARY.

To the east and north-east of the town of Wellington, N.S.W., a series of volcanic and interbedded pyroclastic rocks is exposed. The volcanic series extends from Geurie to Wellington and southwards to Molong and Orange, although only the Wellington area is discussed. It can be correlated with andesites at Blayney and Lucknow and with similar rock types in the Forbes-Parkes district.

Lava types examined petrographically have been classed as trachyandesites, andesites, basalts and trachybasalts and these show genetic relations with sills of augite lamprophyre which occur about 10 miles east of Wellington and which are intruded into the Silurian strata.

A feature of the lavas is their widespread alteration and the presence of many veins and vugs which are attributed to deuteric activity during extrusion. The lavas are interbedded with tuffs, breccias and agglomerates which are for the most part closely related to the lava types. Cognate and other xenoliths occur frequently in the flows.

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STUDIES IN THE INHERITANCE OF RESISTANCE TO RUST OF BARLEY.

PART II.

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INTRODUCTION.

In an earlier paper in these *Proceedings* (Waterhouse, 1927), results from several crosses between barley varieties were presented which showed that a single dominant genetic factor determined resistance to *Puccinia anomala* Rostr., the cause of barley leaf rust. There was no evidence of linkage with factors determining certain morphological characters studied.

Although much genetical work on barley has since been reported, there are apparently no records of other work on inheritance of rust resistance. The work now presented deals with a continuation of the original studies and carried forward between the years 1924 and 1941. An extensive programme of work had been planned. It later became impossible to carry it through to completion, and as it is now not intended to continue the barley work, it seems wise to make the results obtained available to other workers.

MATERIALS AND METHODS.

With a few additions, the barley varieties already classified for resistance (Waterhouse, 1927) were used. Pots of seedlings were inoculated in the usual way and the rust reactions in the plant house determined on the scale generally adopted. Parent varieties were used for direct comparison with the cross-bred material sown at the same time and kept under comparable conditions. This is necessary because alterations in the environmental conditions change the reactions shown in certain cases; this applies particularly to the group of barleys classified as being "moderately resistant" to *P. anomala*. Reactions recorded in May as "2" change to "4" in February, when much higher temperatures prevail: intermediate reactions like "2+", "X" and "4°" are shown under intermediate conditions of light and temperature. Many of the "resistant" varieties exhibited no such variation, remaining resistant and showing "O" (flecks) under all the temperature conditions tested.

Crosses were made in the field. F₁ plants after being tested in pots in the plant house were transplanted to open plots and grown to maturity. The same was done with the back-cross and certain of the F₂ plants used in the F₃ tests; others of these were grown from grain sown directly in the open—not tested as F₂ individuals.

The culture of *P. anomala* used was the same as that reported upon previously. During the period, nine cultures derived from a number of sources were tested on an empirically selected group of "moderately resistant" and "resistant" varieties, but no departure from the behaviour shown by the stock culture was found. At the time, the set of differential varieties worked out by D'Oliveira had not been obtained.

For the stem rust tests, the standard cultures maintained for the wheat rust work were used on the barleys.

EXPERIMENTAL RESULTS.

(a) Tests with *P. anomala*.

F1 Results.

1. Crosses were made between two susceptible parents as follows :

Parents.				No. of Seedlings Tested.
Kinver	× Pryor	23
"	× Cape	10
"	× Skinless	14
"	× Trabut	2
Cape	× Kinver	4
"	× Skinless	13
"	× C.I. 2329	3
"	× Peatland	14
Skinless	× Success	11
"	× Bel. 2071	5
Volga	× <i>Hordeum spontaneum</i>	9
"	× Reka	7
Reka	× Volga	6
C.I. 2309	× C.I. 2222	23
"	× Cape	8
Golden Grain	× Mariout	3
Luth	× C.I. 2237	16

In all cases the F1 plants were susceptible ; no difference between their reactions and those of the parents could be detected.

2. One cross between two "moderately resistant" parents was made.

Minn. II 20.10B × Minn. II 21.14 gave seedlings showing a "2+" reaction similar to that of the parents tested at the same time.

3. Crosses between two "resistant" parents were made as follows :

Parents.				No. of Seedlings Tested.
Minn. II 21.15	× O.A.C. 21	12
"	× Manchuria	12
Minn. II 21.17	× O.A.C. 21	31
"	× Manchuria	15
Manchuria	× Minn. II 21.17	19
"	× Virginia Hooded	5
O.A.C. 21	× Manchuria	18
"	× Virginia Hooded	2
Virginia Hooded	× Manchuria	6

The reactions of the parents showed variations from "0" (flecks) to "1" reactions within the same pot. No differences of any significance were shown by the F1 plants.

4. Crosses between a "resistant" and a "moderately resistant" parent were made as follows :

Parents.				No. of Seedlings Tested.
Minn. II 21.15	× Minn. II 21.14	15
Minn. II 21.14	× Minn. II 21.15	15
O.A.C. 21	× California Feed	27
Virginia Hooded	× Success	1

In these cases the F1 reactions were not significantly different from the "0" to "1" reactions of the resistant parent.

5. Crosses between a susceptible and a "moderately resistant" parent were made as follows:

Parents.		No. of Seedlings Tested.
Cape	× California Feed	15
Skinless	× "	12
Kinver	× "	23
Minn. II 20.10B	× Kinver	23
"	× Minn. II 21.14	4
Minn. II 21.14	× Kinver	10
Marionet	× Skinless	15
Minn. I 16.13	× Kinver	15
Coast	× "	14
Sahara 3770	× "	24
Locride	× "	11
Psaknon	× "	16
Orge Fourragère	× "	13

The F1 reactions were of the "2+" type, being practically the same as those of the "moderately resistant" parents. These, as pointed out earlier, give reactions that are subject to considerable variation with temperature change: in mid-summer the reaction has to be classed as "4". In a few cases F1 tests were made under these conditions, and then the reactions were also of the "4" type.

6. Crosses between a susceptible and a "resistant" parent were made as follows:

Parents.		No. of Seedlings Tested.
Minn. II 21.15	× Skinless	10
"	× Cape	9
Cape	× Minn. II 21.15	12
Minn. II 21.17	× Skinless	30
Skinless	× Minn. II 21.17	11
C.I. 2208	× C.I. 2209	10
"	× C.I. 2237	19
"	× Skinless	25
Skinless	× C.I. 2208	26
C.I. 2220	× Skinless	8
Skinless	× C.I. 2220	6
C.I. 2220	× C.I. 2222	12
Manchuria Sel. C163	× Skinless	14
Skinless	× Manchuria Sel. C163	35
Manchuria Sel. C163	× Cape	30
"	× Manchuria Sel. C225	15
"	× Kinver	19
"	× Manchuria Sel. C81	13
O.A.C. 21	× Skinless	50
Skinless	× O.A.C. 21	28
O.A.C. 21	× Cape	45
Virginia Hooded	× Volga	27
Volga	× Virginia Hooded	5
Virginia Hooded	× Luth	46
"	× Intermediate	43
"	× Weider	14
"	× Bel. 2071	13
Colsess	× Skinless	29
Manchuria	× Pryor	28
"	× Cape	19
Manchuria Sel. C168	× "	3
No. 22	× "	17
Minn. II 21.18	× Pusa No. 1	5
Bolivia	× Cape	12
Weider	× Skinless	9
Skinless	× Weider	11

The reaction of the "resistant" parents varied from "0" to "1" and was hardly distinguishable, if at all, from those shown by the F1 plants.

Summary of the F1 Results.

The evidence shows that there is dominance of resistance² to *P. anomala*. This applies to the "resistant", as well as the "moderately resistant" varieties from whatever source.

Back-cross Results.

1. A back-cross between Skinless and the F1 of (Skinless \times Manchuria Sel. C163) gave a total of 12 plants resistant, showing reactions "0" to "1" and 11 plants susceptible, showing "4" reactions. Progenies of only 5 of these plants were available for further tests. Three from susceptible parents gave a total of 258 tested plants, all of which were susceptible. The other 2 came from resistant plants; one gave 34 resistant and 14 susceptible plants and the other 36 resistant and 12 susceptible plants.

2. Skinless \times (Skinless \times O.A.C. 21) yielded 17 resistant and 23 susceptible seedlings.

3. Pryor \times (Pryor \times Manchuria) gave 6 resistant and 7 susceptible plants.

4. Minn. II 21.14 \times (Minn. II 21.14 \times Minn. II 21.15) gave 4 resistant and 5 susceptible plants.

The numbers of individuals dealt with are small, but the results point to a single dominant factor for resistance operating.

*F2 Results.**1. Crosses between Two Resistant Parents.*

(a) A cross between O.A.C. 21 and Minn. II 21.17 gave 208 plants classified as "0" to "1", these being similar to the reactions of each parent.

(b) The cross Manchurian \times Minn. II 21.17 yielded 224 resistant seedlings classified as "0" to "1", similar to the parent reactions.

(c) The cross Manchurian \times O.A.C. 21 yielded 245 resistant plants similar in resistance to the parents.

2. Crosses between "Resistant" and "Moderately Resistant" Parents.

The results may be summarized in the following table:

Parents and Their Reactions.	Counts of F2 Plants.				Deviation from 3 : 1 Ratio.
	Re-sistant.	Re-action.	Moderately Resistant.	Re-action.	
Californian Feed, "2+" \times O.A.C. 21, "0" to "1".	157	"0" to "1"	55	"2+" to "X"	2
Minn. II 21.14, "4c" \times Minn. II 21.15, "0" to "X".	171	"0" to "X"	61	"4c"	3
Minn. II 21.15, "0" to "X-" \times Minn. II 21.14, "4c".	149	"0" to "X"	48	"4c"	1
Minn. II 21.14, "4c" \times Manchuria, "0" to "X-".	196	"0" to "X"	67	"4c"	1
Cape, "2+" \times O.A.C. 21, "0" to "1".	142	"0" to "1"	40	"2+"	5
Minn. II 21.15 "0" to "1" \times Cape "2+".	72	"0" to "1"	18	"2+"	5
Cape, "2+" \times Manchuria Sel. C163 "0" to "1".	137	"0" to "1"	37	"2+"	6

The results show the operation of a single dominant factor determining "resistance".

3. Crosses between "Moderately Resistant" and Susceptible Parents.

The results may be summarized as follows :

Parents and Their Reactions.	Counts of Plants.				Deviation from 3 : 1 Ratio.
	Moderately Resistant.	Re-action.	Sus-ceptible.	Re-action.	
Cape, "4c" × Californian Feed, "X"	165	"X"	52	"4c"	2
Kinver, "4" × Californian Feed, "X"	67	"X"	19	4	2
Kinver, "4" × Minn. II 21.14, "X+	111	"X+"	35	4	2
Kinver, "4" × Marionet, "X"	83	"X"	34	4	5
Kinver, "4" × Sahara 3770, "X"	174	"X"	66	4	6
Kinver, "4" × Psaknon, "X"	52	"X"	18	4	1

The results show the operation of a single dominant factor determining "moderate resistance".

4. Crosses between "Resistant" and Susceptible Parents.

The results may be summarized as follows :

Parents and Their Reactions.	Counts of F2 Seedlings.				Deviation from 3 : 1 Ratio.
	Re-sistant.	Re-action.	Sus-ceptible.	Re-action.	
Skinless, "4" × Minn. II 21.15, "0" to "1"	173	"0" to "1"	54	4	3
Minn. II 21.15, "0" to "1" × Skinless "4"	137	"0" to "1"	44	4	1
Skinless, "4" × Minn. II 21.17, "0" to "1"	313	"0" to "1"	120	4	12
Skinless, "4" × C.I. 2208, "0" to "1"	158	"0" to "1"	65	4	9
C.I. 2208, "0" to "1" × Skinless "4"	149	"0" to "1"	59	4	7
Skinless, "4" × C.I. 2220, "0" to "1"	22	"0" to "1"	7	4	—
Skinless "4" × Manchuria Sel. C163, "0" to "1"	182	"0" to "1"	62	4	1
Manchuria Sel. C163, "0" to "1" × Skinless "4"	239	"0" to "1"	78	4	1
O.A.C. 21, "0" to "1" × Skinless "4"	208	"0" to "1"	82	4	9
Cape, "4" × Minn. II 21.15, "0" to "1"	26	"0" to "1"	14	4	4
Cape, "4" × O.A.C. 21, "0" to "1"	194	"0" to "1"	47	4	13
Kinver, "4" × Manchuria Sel. C163, "0" to "1"	63	"0" to "1"	19	4	2
Totals	1,864		651		22

In all cases the deviation from the expectancy for a 3 : 1 ratio is less than twice the S.E. The results show the operation of a single dominant factor for resistance.

In three of the crosses, the F₂ plants after testing were grown to maturity and their morphological characters determined in regard to beard, hulled grain and smooth awn. Rust resistance was inherited independently of any of these features.

F₃ Results.

Progenies of three of the crosses studied in the F₂ were examined with the following results :

Parents of Cross.	Classification of F ₃ Families.					
	Homo-zygous Re-sistant.	Average No. of Plants Tested.	Hetero-zygous Re-sistant.	Average No. of Plants Tested.	Homo-zygous Sus-ceptible.	Average No. of Plants Tested.
(a) Skinless × Minn. II 21.15	56	26	98	24	52	19
Expectancy ..	51.5		103		51.5	
(b) Cape × Minn. II 21.15	6	20	21	27	10	25
Expectancy ..	13.25		26.5		13.25	
(c) Skinless × Minn. II 21.17	20	29	40	25	27	31
Expectancy ..	21.75		43.5		21.75	

Summation of Individuals in the Heterozygous F₃ Families.

Parents of Cross.	Resistant.	Susceptible.	Deviation from 3 : 1 Ratio.
Skinless × Minn. II 21.15	1,802	612	8
Cape × Minn. II 21.15	409	160	18
Skinless × Minn. II 21.17	759	248	4
Total	2,970	1,020	22

In all cases the deviation from the expectancy on a 3 : 1 basis is less than twice the S.E.

Again there is clear evidence of the operation of a single dominant factor for resistance.

Summary of Leaf Rust Results.

The evidence from the F₁, back-cross, F₂ and F₃ results points clearly to resistance depending upon a single dominant gene. The crosses used involved parents from widely scattered areas. There is nothing in the evidence to show that it is not the same gene in the many varieties used. Additional crosses

between resistant sorts would be necessary to complete the evidence. This barley leaf rust result is entirely different from that obtained in the wheat leaf rust studies (unpublished data) where at least two major genes operate.

(b) *Tests with Puccinia graminis tritici.*

Seedling tests in the plant house do not give anything like the clear-cut reactions that are obtained with *P. anomala*; varieties which are quite susceptible show a considerable amount of chlorosis; this is general. The pustule size is the chief distinguishing feature. Again, temperature changes bring about marked alterations in the reactions. Thus a "2" in winter may increase to a "2 $\frac{1}{2}$ " reaction in summer; the latter pustule is quite a large one with considerable uredospore formation on the chlorotic areas.

Varieties were classified on the basis of their reactions to the three races of *P. graminis tritici* numbered 34, 43 and 45, as well as to *P. anomala*. Under the conditions prevailing at the time of the test, some varieties gave only "1=" reactions; the reaction "2" was taken as setting the upper limit to the resistant class. It was sometimes difficult to determine whether a "2" reaction was significantly different from a "2+" reaction which was taken as the lower limit in the susceptible class.

Based on such "resistance" and "susceptibility", 13 of the 16 possible groupings were found, as follows:

1. *Resistant to P. anomala and P. graminis tritici races 34, 43, 45.*
Virginia Hooded, Coast.
2. *Susceptible to P. anomala and P. graminis tritici races 34, 43, 45.*
Luth, C.I. 2222, Trabut, Mariout, Volga, Standwell, Hero, Intermediate, Pearl, Chedret, Coutsopodi, Janina, Sahara 3764, Sahara 3765, Burton's Malting.
3. *Resistant to P. anomala and Susceptible to P. graminis tritici races 34, 43, 45.*
Minn. II 21.15, Minn. II 21.17, Manchuria Sel. C168, Manchuria Minn. 184, Manchurian, O.A.C. 21, No. 22, Orge 4th.
4. *Susceptible to P. anomala and Resistant to P. graminis tritici races 34, 43, 45.*
C.I. 2256, C.I. 2269, C.I. 2209, C.I. 2210, C.I. 2237, C.I. 2280, C.I. 2226, C.I. 2228, Manchuria Sel. C225, Cape, Kinver, Golden Grain, Albert, Princess, Goldthorpe, Tunis, Gatama, Roseworthy Oregon, Squarehead.
5. *Resistant to P. anomala and P. graminis tritici 34 and 45, and Susceptible to P. graminis tritici 34.*
C.I. 2220.
6. *Resistant to P. anomala, P. graminis tritici 43, 45 and Susceptible to P. graminis tritici 34.*
C.I. 2208, Manchuria Sel. C163, Colsess, Orge Fourragère.
7. *Resistant to P. anomala and P. graminis tritici 45 and Susceptible to P. graminis tritici 34, 43.*
Minn. II 21.18, No. 305, Orge 14J.
8. *Susceptible to P. anomala and P. graminis tritici 34 and Resistant to P. graminis tritici 43, 45.*
Black Russian, C.I. 2206, Nepal, C.I. 2254, Gold, Salonika, Sahara 3766, Sahara 3768, Gisborne, Tennessee Winter, Hanchen.
9. *Susceptible to P. anomala and P. graminis tritici 43 and Resistant to P. graminis tritici 34 and 45.*
C.I. 2213, C.I. 2215, C.I. 2217, Zea.
10. *Susceptible to P. anomala and P. graminis tritici 45 and Resistant to P. graminis tritici 34, 43.*
C.I. 2229, Nodding Barley.

11. *Susceptible to P. anomala and P. graminis tritici 34, 43 and Resistant to P. graminis tritici 45.*

C.I. 2204, C.I. 2214, C.I. 2219, C.I. 2221, Manchuria Sel. C81, Skinless, Pryor, Reka, *H. spontaneum*, Purple Hull-less, Shorthed, Chilian, Kaylaria, Sahara 3767, Sahara 3769, Erect Eared Barley, Himalaya, Orzo Nuda Putignans, Orzo Maraina, White Hull-less, Duckbill, Garton's Regenerated Maltster.

12. *Susceptible to P. anomala and P. graminis tritici 34, 45 and Resistant to P. graminis tritici 43.*

No. 78, Larissa.

13. *Susceptible to P. anomala and P. graminis tritici 43, 45 and Resistant to P. graminis tritici 34.*

No. 49, Primus, Meloy.

F1 TESTS OF RESISTANCE TO *P. GRAMINIS TRITICI*.

A number of crosses were made for these studies, based upon the reciprocal reactions shown to the four rusts. The F1 plants were tested and grown to maturity. It then became impossible to prosecute the studies, and later generation tests could not be made.

In the F1 tests of 37 crosses selected for their reciprocal resistance and susceptibility, there was dominance of resistance to race 43, and of susceptibility to races 34 and 45. No correlation with resistance to *P. anomala* was found. This also applied to three of the crosses in which resistance to *Erysiphe graminis hordei* was also involved.

RESISTANCE OF *ERYSIPHE GRAMINIS HORDEI*.

The occurrence of powdery mildew in the planthouse led to inoculation tests being carried out for resistance to *E. graminis hordei*. Later this was checked by recording the field behaviour in respect of the disease.

The following varieties were found to be resistant: C.I. 2269, C.I. 2215, C.I. 2237, C.I. 2280, C.I. 2218, C.I. 2250, Lion, No. 22, Psaknon, White Hull-less, Bolivia, C.I. 2329, Juliaca, Coast, Portuguese, Goldfoil, Hanna, Bark, Bolivia, Bel. 2071, Duplex, 017, Kwan, Weider.

SUMMARY.

Further studies are reported of resistance to leaf and stem rusts, and to a small extent to powdery mildew of barley.

Numerous F1 tests, with fewer back-cross, F2 and F3 studies, confirm the action, in the crosses studied, of a single dominant factor for resistance to *P. anomala*. This applies to varieties obtained from widely scattered sources.

Many F1 tests showed dominance of resistance to *P. graminis tritici* race 43, and of susceptibility to races 34 and 45 of this rust.

In the cases studied there was no evidence of correlation between leaf and stem rust or with certain morphological characters that were examined.

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CORROSION OF SURFACES HEATED ABOVE THE BOILING POINT OF THE CORRODANT.

By R. C. L. BOSWORTH, D.Sc., F.A.C.I.

Manuscript received, September 17, 1947. Read, October 1, 1947.

The process of matter loss which occurs during the corrosion of metals appears to be controlled by many physical factors analogous to those which control the convective heat loss from geometrically similar hot bodies. When the temperature of a hot body immersed in a liquid is steadily raised beyond the boiling point of the liquid the curve of the emittance, and therefore the rate of boiling, plotted against the temperature takes a characteristic form. With rising temperature just beyond the boiling point there is first a steady rise in the emittance. At a certain temperature, however, a change occurs from film to nuclear boiling with an associated sudden drop in the emittance, which thereafter steadily rises with rising temperature. The work described in this note sets out to see if the rate of loss of matter by corrosion shows a similar behaviour when the temperature of the body subject to corrosion is slowly raised past the point at which nuclear boiling commences.

THE EXPERIMENTAL METHOD.

In the experimental measurement of corrosion from surfaces heated above the boiling point of the corrodatant a hot wire device was used. The wire was heated by means of an electric current to a temperature which could be measured from the electrical resistance. Further, the rate of corrosion could be measured in terms of the rate of change of this resistance.

The wires examined were copper, the corrodatants glacial acetic acid and acetic anhydride. A 5 cm. length of fine wire (38-46 gauge S.W.G.) was clamped on to current leads of the same metal. The clamps also held lighter voltage leads of the same metal. The specimen with its four leads was mounted in a cork stopper which fitted into a wide test tube containing the corrodatant under examination. The test tube was mounted in a thermostatic bath maintained at the boiling point of the corrodatant. The heating current was passed through a controlling resistance, an ammeter and the wire under test; and thus served to heat the wire above the boiling point of the corrodatant and cause the liquid to boil on the wire. A voltmeter connected across the voltage leads enabled the resistance of the wire to be read. The quotient of the resistance obtained with the normal heating current over the resistance obtained with a very small current (of the order of 10 milliamps.) is a measure of the temperature (θ) above the boiling point of the liquid.

THEORY OF THE METHOD.

In an experimental run three measurements are taken—the time, the current I and the voltage drop V . The resistance R ($=V/I$) is related to the specific resistance (ρ) of the wire at the operating temperature T , and the radius (r) of the wire by

$$R = \frac{5\rho}{\pi r^2} \dots\dots\dots (1)$$

5 being the length (in cms.) of the heated wire. For a change dr in the radius

of the wire a volume $2\pi r dr$ is lost from every unit length of the wire. The rate of corrosion q (in units of grams per sq. cm. per sec.) is then given by

$$q = \delta \frac{dr}{dt} \dots\dots\dots (2)$$

where δ is the density of the material of the wire. By substituting equation (2) in equation (1) we obtain

$$q = \delta \sqrt{\frac{5\rho}{\pi}} \frac{d(R^{-1/2})}{dt} \dots\dots\dots (3)$$

The quantity R , it should be recalled, is the resistance of a 5 cm. length of wire. From equation (3) we see that, provided the corrosion proceeds at a constant rate as the wire thins, the quantity $R^{-1/2}$ should vary linearly with the time.

The heat generated per unit surface area by the electric current is proportional to $I^2 R^{3/2}$, and provided this factor is kept constant as the wire thins we may expect a constant surface temperature. (It seems reasonable to assume that the thermal transmittance will not vary as corrosion proceeds.)

EXPERIMENTAL RESULTS.

The samples examined were heated by various currents up to 20 amperes. On any fixed run the quantity $I^2 R^{3/2}$ was kept constant, and $R^{-1/2}$ plotted against the time. Any given run was continued until either there was a ten per cent. change in the resistance or else the wire had fused. From the resistance measurements corrosion rates and temperatures were derived by the methods outlined above. The derived corrosion rates and temperatures (excess above the boiling point) are shown in the two figures. Figure 1 refers to copper in glacial acetic acid, and Figure 2 to copper in acetic anhydride.* It will be seen that the corrosion rates are quite large at the boiling points and rise steadily with further increase in the temperature, until, for temperatures of the order of 60° C. to 80° C. above the boiling point there is a sudden drop in the rate of corrosion, particularly in the case of acetic anhydride in which the rate of corrosion when the wire is 80° C. above the boiling point is only a small fraction of that when the wire is at the boiling point. Associated with this change in the rate is an equally obvious change in the chemistry of the reaction. At the lower temperatures copper dissolves to give a cupric salt which forms an intensely blue coloured complex with acetic anhydride. As soon as the temperature reaches the point at which the corrosion rate shows the sudden drop the blue colour begins to disappear and in its place there appears first a yellowish muddy fluid and finally a flocculent pink precipitate, apparently cuprous oxide or a basic cuprous acetate. Once the pink precipitate has formed no further corrosion apparently takes place and the supernatant liquid remains colourless. This is particularly remarkable in that the leads, which are not protected by a vapour film and have a surface area exposed to the liquid much larger than that of the hot wire, also appear to cease dissolving in the corrodant when attack on the hot wire ceases.

DISCUSSION.

There are two points of interest in this work. In the first place it appears that a copper heating surface in acetic anhydride may be protected from corrosion if the temperature of the copper is high enough. One might compare this phenomenon with the drop in heat transfer coefficient which occurs when the temperature of a heating surface is made sufficiently high (see for example

* The corrosion rate in these two figures is measured in the customary units of mgrms. dec.⁻¹ day⁻¹.

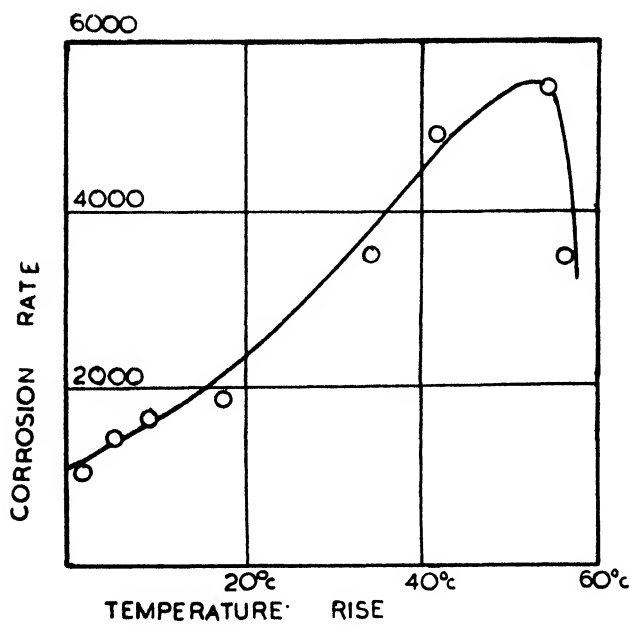


Fig. 1.

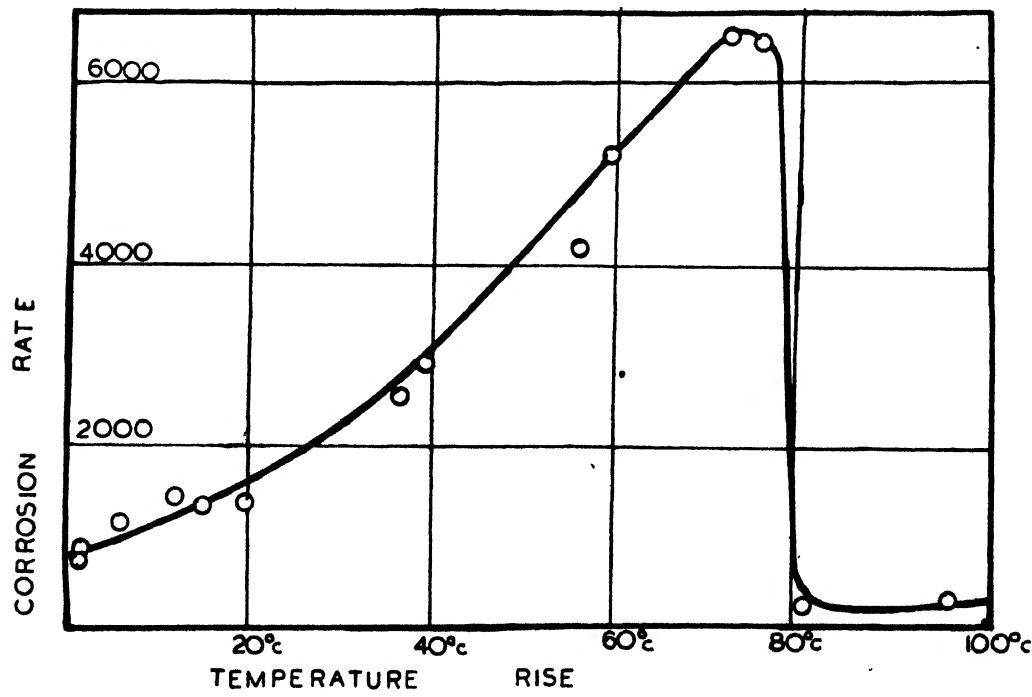


Fig. 2.

Bosworth, 1946). Presumably the same cause is responsible for both phenomena, namely the formation of a complete vapour film over the surface.

In the second place these experiments give an interesting indication of the part played by the equilibrium between the cuprous and the cupric ions in the corrosion of copper. This subject has been treated by Gatty and Spooner (1938). In the oxidative reaction



dissolved oxygen acts as the electron acceptor. The reverse reaction will only proceed at an appreciable rate heterogeneously at an interface. When this occurs at a copper-electrolyte interface a corrosive reaction is involved, namely



It now appears that when the copper surface is covered with a vapour film, the reverse of equation (A) occurs at the vapour liquid interface leading to the reduction of cupric to the cuprous state without progressive attack on the copper surface.

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A NEW METHOD FOR THE COMPARISON OF THE THERMAL CONDUCTIVITIES OF FLUIDS.

PART II.

By R. C. L. BOSWORTH, D.Sc., F.A.C.I.

Manuscript received, September 17, 1947. Read, October 1, 1947.

SCOPE OF THE INVESTIGATION.

In Part I of the series of papers on this subject (Bosworth, 1947) it was shown that the relative thermal conductivities and convective moduli of fluids could readily be obtained from a series of measurements of the rate of heat loss (q) and the excess temperature (θ) when a hot wire is immersed successively in the fluids to be compared. The quantity q/θ is plotted against $\theta^{1/3}$. The points for any one fluid and given hot wire when thus plotted were shown to fall on a straight line. With a given wire the intercepts on the q/θ axis were shown to be proportional to the thermal conductivities (k) of the fluids under test, while the slopes were shown to be proportional to $ka^{1/3}$, where a , the convective modulus, is related to other physical properties of the fluid by

$$a = \frac{\rho^2 c g \beta}{\eta k} \dots\dots\dots (1)$$

with ρ the density,
 c the heat capacity at constant pressure,
 β the coefficient of volumetric expansion,
 η the viscosity, and
 g the acceleration due to gravity.

The heat loss factor for a resistance wire heated by an electric current (I) is directly proportional to I^2 , while θ the excess temperature may readily be measured by using a thermocouple with one junction on the surface of the wire and one immersed in the fluid.

Instruments of this type were used in comparing the thermal conductivities and convective moduli of a number of common fluids with the corresponding properties of water. Except for the more volatile fluids the relative figures obtained by this method were found to be in satisfactory agreement with the best figures from the literature. Since the method is essentially a comparative one, it was suggested that it would be of outstanding value in the measurement of the thermal conductivities of binary mixtures.

The present paper takes up the subject with the study of the thermal conductivity and convective moduli of aqueous solutions of potassium chloride, sucrose and glycerine at 27° C., and obtains, for each of the systems, the properties above as a function of the concentration.

An empirical equation connecting the thermal conductivity (k) of a binary mixture of fluids with the thermal conductivities (k_1) and (k_2) of the components has been given by Barratt and Nettleton (1929). Their equation reads:

$$k \sinh 100\mu = k_1 \sinh p\mu + k_2 \sinh (100-p)\mu \dots\dots\dots (2)$$

where p is the weight percentage of the first component and μ is a factor which varies with the constituents and the temperature. A table of the values of μ

given by Barratt and Nettleton has been amended by Bates, Hazzard and Palmer (1938), who also found equation (2) to give satisfactory accounts of the thermal conductivity of liquid mixtures. In assessing the value of the method of measurement under examination we thus have three independent modes of comparison; published data for the thermal conductivities of the mixture, empirical equation (2) and the fact that the various properties entering into the determination of the convective modulus are, with the exception of the thermal conductivity, comparatively well known, so that it is possible to check the method for self consistency by independent measurements of the thermal conductivity and the convective modulus.

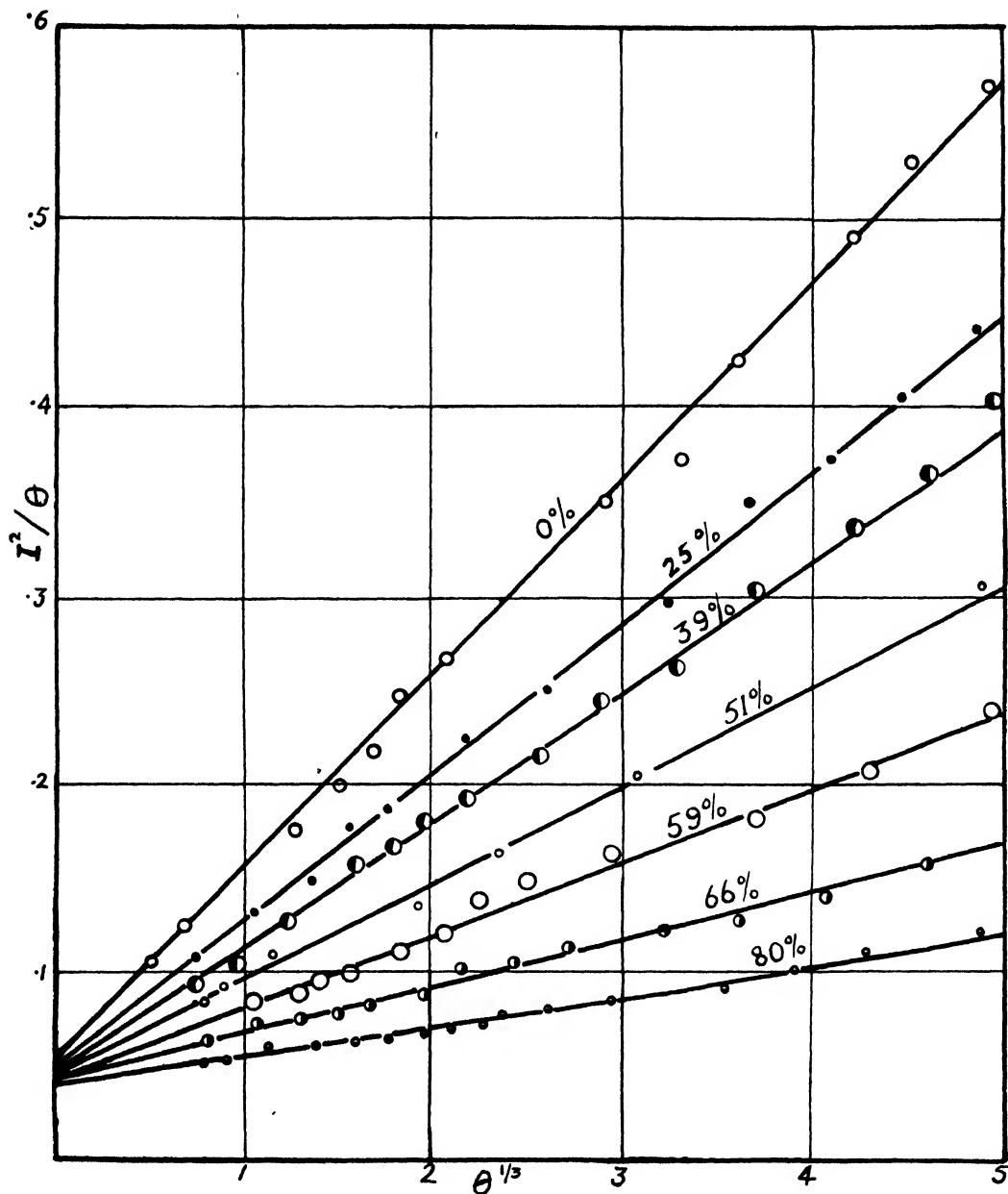


Fig. 1.

EXPERIMENTAL RESULTS.

The experimental arrangements and procedure were the same as that described in the earlier paper (Bosworth, 1947). Results were first obtained as a series of readings of I versus θ . Data for any particular system were then plotted in the form of I^2/θ versus $\theta^{1/3}$. Figure 1, for example, shows the data obtained from a series of sucrose solutions plotted in this way. The top (and steepest) curve refers to the results from pure water and the others in order refer to 25%,

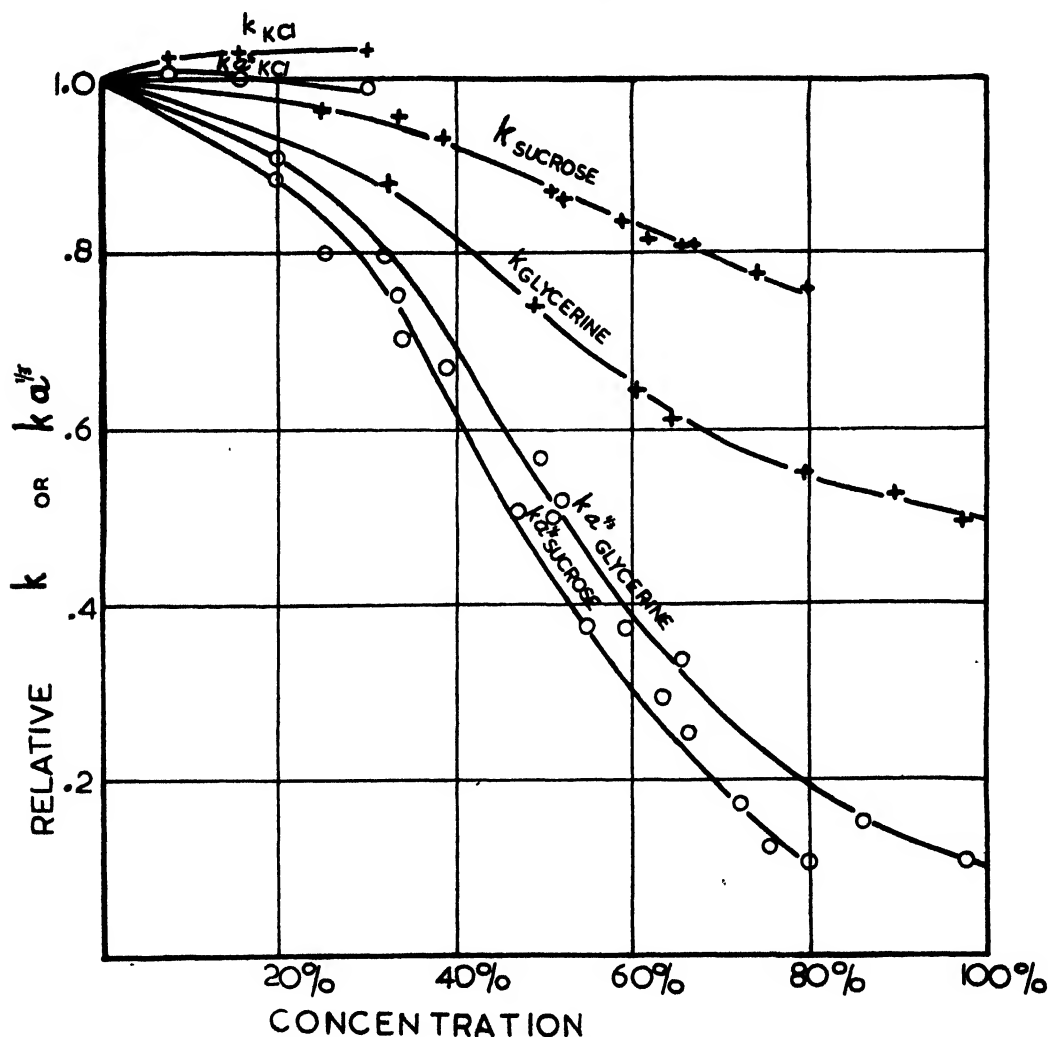


Fig. 2.

39%, 51%, 59%, 66% and 80% sucrose solutions, all at 27° C. and all expressed as weight per cent. of sucrose on the weight of the solution. The lowest curve (80%) refers to a metastable (supersaturated) solution. No detectable crystallization took place during the determinations, but the solution crystallized on standing afterwards.

A similar series of curves were obtained for solutions of potassium chloride in water and for mixtures of water and glycerine. The completed data from these three sets of determinations are shown in Figure 2, where curves are given for the variation of the intercepts and slopes plotted against the weight per-

centage composition of the fluid for all three systems. The points marked with crosses refer to the intercepts (or relative thermal conductivities) and those with circles to the slopes (proportional to $ka^{1/3}$). In the KCl system it will be seen that the addition of the salt increased the thermal conductivity by about 3%, while the addition of the other two substances lowered the thermal conductivity. The slopes were all decreased with increasing concentration of the solute except in the case of the more dilute KCl solutions where the slope is slightly greater than unity for ranges of concentration up to 15% KCl.

DISCUSSION OF THE SYSTEM KCl-WATER.

Figures for the relative thermal conductivities and convective moduli at various concentrations have been calculated from the data given in Figure 2. The results are tabulated in Table I.

TABLE I.

Relative Thermal Conductivities and Convective Moduli for KCl Solutions.

Concentration Wt. %.	Relative Thermal Conductivity.	Relative Convective Moduli.
0.0	1.000	1.000
5	1.020	0.96
10	1.025	0.94
20	1.030	0.90
30	1.030	0.85

The slight rise in the thermal conductivity produced by the addition of KCl to water has been recorded before (*International Critical Tables*, Vol. V (1928)). The fall in the convective modulus with increase in concentration is, primarily, a consequence of the increase in viscosity with increasing concentration. Thus the viscosity of a 30% solution of KCl at 25° C. is given in the *International Critical Tables* as some 15% higher than that of pure water, while the table above shows that the convective modulus is 15% lower.

DISCUSSION OF THE SYSTEM SUCROSE-WATER.

Values of the relative thermal conductivity and convection modulus of sucrose solutions are given in Table II as a function of the concentration. There

TABLE II.

Relative Thermal Conductivities and Convective Moduli of Sucrose Solutions at 27° C.

Concentration Wt. %.	Relative Thermal Conductivity.	Relative Convective Modulus from	
		Measurement.	Calculation.
0	1.00	1.00	1.00
20	0.98	0.70	0.57
40	0.93	0.31	0.27
50	0.88	0.17	0.17
60	0.83	0.070	0.056
80	0.76	0.0020	0.0021

are four columns in this table. The first gives the concentration, expressed as a weight per cent., the second the relative thermal conductivity calculated from Figure 2, the third the relative convective modulus calculated from the same source, and the fourth the relative convective moduli calculated from the thermal conductivities given in column 2 combined with the other physical properties: densities, specific heats, coefficients of thermal expansion and viscosities. The figures for the viscosities were taken from the International Critical Tables and, for the more concentrated solutions from Lyle (1941); the specific heats were calculated from the formula of Yanovsky and Archangelsky (1928) and the densities and the coefficients of thermal expansion were calculated from the tables of Spencer and Meade (1945).

The excellent agreement between the figures in columns 3 and 4 may be taken as confirming the accuracy of the experimental figures given in column 2. However, the thermal conductivity versus composition curve cannot be made to follow any expression of the type of equation (2). The change in thermal conductivity produced by the addition of a small amount of extra sucrose to a dilute solution is less than that produced by the addition of the same quantity to a concentrated solution.

DISCUSSION OF THE SYSTEM GLYCERINE-WATER.

This system has been studied from 100% water to 100% glycerine. All the relevant data at 27° C. may be obtained from Figure 2. A summary of these results is given in Table III, which includes columns of measured and of calculated figures.

TABLE III.

Relative Thermal Conductivities and Convective Moduli of the Binary System Glycerine-Water at 27° C.

Concentration Wt. % Glycerine.	Relative Thermal Conductivity from		Relative Convective Modulus from	
	Measurement.	Calculation.	Measurement.	Calculation.
0	1.00	1.00	1.00	1.00
20	0.94	0.87	0.79	0.79
40	0.82	0.75	0.57	0.60
50	0.73	0.69	0.42	0.49
60	0.64	0.65	0.26	0.30
80	0.55	0.56	0.064	0.076
100	0.48	0.48	0.0076	0.0052

The figures in column 2 are the relative intercepts from Figure 2. The figures in column 3 were calculated from a formula of the Barratt and Nettleton type using the revised values of the constants given by Bates, Hazzard and Palmer (1938). It will be seen that while the agreement is excellent at the higher concentrations, it is not so at the lower concentrations. Once again these results have indicated a relatively smaller change of thermal conductivity with concentration change in the more dilute solutions. The calculated convective moduli, given in column 5 above, were obtained from thermal conductivities from column 2, data for density and coefficient of thermal expansion from Bosart and Snoddy (1928), data for viscosity from Shelly (1932), and for the specific heats from the International Critical Tables. The agreement with the measured

convective moduli is excellent and the suggestion made originally that this particular method of measurement should be very suitable for binary mixtures appears to be amply justified.

SUMMARY.

The thermal conductivities and convective moduli of binary solutions of KCl-water, sucrose-water and glycerine-water at 27° C. have been measured as a function of the concentration by the method described in the first paper of this series. The results are shown to be self consistent in that values of the convective modulus calculated from the measured thermal conductivity and the generally accepted values of other physical properties of the solutions are in excellent agreement with those obtained by direct measurement.

In the case both of sucrose-water and of glycerine-water the addition of further solute produces a relatively larger change in the thermal conductivity of the more concentrated solutions.

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PART IV

THE CHEMISTRY OF BIVALENT AND TRIVALENT IRIIDIUM.

PART IV. THE OXIDATION-REDUCTION POTENTIAL OF THE BROMIRIDATE-BROMIRIDITE SYSTEM.

By F. P. DWYER, D.Sc.,
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and R. S. NYHOLM, M.Sc.

Manuscript received, October 9, 1947. Read, November 5, 1947.

In a previous communication (Dwyer, McKenzie and Nyholm, 1944) it was shown that the chloriridate-chloriridite system behaved as a typical anionic system, the potential rising with increasing ionic strength. The bromiridate-bromiridite system was similarly expected to be anionic, with the potential at a somewhat lower value owing to the greater stability constant of the bromiridate ion. This was found to be the case, but the chief interest in the system was in a unique phenomenon of reduction of the oxidant at moderate and high ionic strengths.

When solutions of potassium hexabromiridate and hexabromiridite were mixed in hydrobromic acid solution the deep violet colour of the oxidant ion was found to lighten appreciably especially when the acid concentration was high. At the same time the odour of bromine could be detected. Pure potassium bromide and also potassium nitrate in the presence of a little hydrobromic acid also led to lightening of the colour and if sufficient potassium bromide or potassium nitrate were added to the solution almost complete decolorization resulted.

The phenomenon appears to be dependent on the opposite effects of ionic strength on the bromiridate-bromiridite and bromine-bromide systems. The potential of the bromine-bromide electrode (E° , 1.08 volts) falls with increasing ionic strength, while that of the bromiridate-bromiridite system (E° , 0.99 volt) rises with increasing ionic strength. The potentials of the two systems thus approach each other as the ionic strength is increased and finally bromide ion is oxidized to bromine, whilst the violet bromiridate ion is reduced to the pale yellow bromiridite ion.

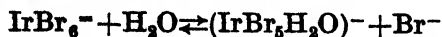
From equilibrium considerations if E'_0 and E''_0 are the respective redox potentials of the bromine-bromide and bromiridate-bromiridite systems, then

$$E'_0 - E''_0 = 0.06 \log \frac{(\text{Br}^-)(\text{IrBr}_6^-)}{(\text{Br}_2)^{\frac{1}{2}}(\text{IrBr}_6^{\equiv})}$$

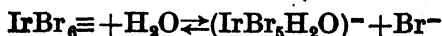
If the ratio of bromiridate and bromiridite ions is kept constant, the reduction of the former will be determined by the potentials of the two systems at the particular ionic strength and by the concentration of bromide ions. If insufficient bromide ion is present, reduction of the bromiridate cannot take place. The concentration of bromide ion arising by dissociation of the bromiridate ion is not sufficient, and solutions of bromiridate in excess of potassium nitrate are quite stable towards reduction.

Freshly prepared dilute solutions of potassium or ammonium hexabromiridate in very dilute hydrobromic acid were violet and gradually changed to indigo blue, but the violet colour could be regenerated by the addition of hydrobromic

acid and a little bromine. This effect could not be produced with other acids and suggests that an aquo compound is formed



Similarly potassium bromiridite prepared by reduction with alcohol in the presence of much hydrobromic acid formed a brownish yellow solution which was oxidized by bromine to the violet bromiridate, but if the solution in dilute hydrobromic acid was allowed to stand it gave the blue compound on oxidation. It thus appears that an equilibrium also exists with the reductant ion



In very weakly acid solutions the potential changes produced by the addition of nitric acid indicated that true hydrolysis (formation of hydroxy complexes) could also occur. Although not mentioned in the original paper, equilibria of this sort undoubtedly exist in solutions of chloriridates and chloriridites. Potassium aque pentachloroiridite has been described by Delepine (1908) and this substance on oxidation gives a dark brown solution of (probably) potassium aquo pentachloroiridate. This latter substance has not yet been described. The potentials quoted for both systems are thus more correctly the potentials of the equilibrium mixtures rather than the simple systems.

EXPERIMENTAL.

Potassium Hexabromiridate.

Black octahedra of this substance were prepared by Gutbier and Priess (1909) by boiling the chloro compound with potassium bromide. The present authors were unable to obtain the substance by this method but found that if the chloro compound were boiled for some hours with hydrobromic acid reduction gradually occurred and the bromo compound could be obtained by oxidizing with bromine in the presence of potassium bromide.

However, in order to avoid contamination with unchanged chloro compound, the substance was finally prepared by refluxing purified potassium hexanitroiridite with concentrated hydrobromic acid and bromine. During the reaction an undescribed nitroso compound appeared to be formed as a reddish crystalline precipitate, especially in the absence of bromine, but finally the solution became deep violet and on cooling deposited black octahedra of the required substance. The identity of this material was checked by X-ray powder photographs, which showed it to be face centred cubic, isomorphous with ammonium chloroplatinate. The substance was finally recrystallized several times in the presence of bromine and a little hydrobromic acid. The solution used in the potential studies was 0.01 M with respect to iridium and 0.028 M with respect to hydrobromic acid.

Potassium Hexabromiridite.

Half of the bromiridate solution was treated with hydrobromic acid and alcohol and evaporated over a water bath, adding more alcohol from time to time. The correct amount of potassium bromide was then added, followed by hydrobromic acid and alcohol. After evaporation to dryness a greenish brown residue was left, which dissolved in dilute hydrobromic acid to a pale brownish yellow solution. This was analysed for iridium and finally adjusted to 0.01 M with respect to iridium and 0.0052 M with respect to hydrobromic acid.

MEASUREMENT OF THE REDOX POTENTIAL.

The apparatus, electrodes and general procedure were similar to those used for the chloriridate-chloriridite system. The temperature of measurement was 20° C. In view of the sensitivity of the system to reduction, the bromiridate was always added last when preparing the various solutions. However, owing to the complex equilibria involved, their slowness of establishment, and the tendency of the solutions to lose bromine, reproducible potentials were difficult to obtain

from different batches of bromiridate and bromiridite. The potentials are thus considered not more accurate than ± 5 mv. The uncertainty in the absolute value of the potentials does not affect the shape of the curves or the general conclusions. Care was taken to obtain the whole of the curves shown with the same batch of oxidant and reductant.

RESULTS.

In the first series of determinations the iridium concentration was kept constant and the concentration of hydrobromic acid varied. The potential rose and then fell away sharply owing to reduction of the oxidant and loss of bromine from the solution (Table I and curve 1).

TABLE I.

Iridium Concentration Constant ($I=0.0030$) and Hydrobromic Acid Concentration Varied

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0033	0.05	0.961
0.0050	0.071	0.989
0.0070	0.084	0.994
0.0100	0.100	0.996
0.0233	0.153	0.991
0.1523	0.390	0.962

In the second series a small constant concentration of bromide and iridium was maintained and the ionic strength raised by the addition of nitric acid (Table IIA and curve 2). The potential rose with increasing ionic strength, but the pronounced falling away at high ionic strengths did not occur. The steep slope at low acidities can be attributed to true hydrolysis. This curve is similar in shape to that obtained for the chloriridate system in hydrochloric acid solution. If extrapolated from the point where hydrolysis becomes serious to infinite dilution, assuming the validity of the Debye Huckel limiting law, an approximate value of 0.990 ± 0.005 volt for the redox potential at infinite dilution is obtained.

TABLE IIA.

Iridium Concentration Constant ($I=0.0060$), Bromide Ion Concentration Constant ($I=0.0006$), Nitric Acid Concentration Varied.

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0065	0.081	0.970
0.0082	0.091	0.988
0.0098	0.099	0.998
0.0149	0.122	1.007
0.0182	0.135	1.008
0.0232	0.153	1.010
0.0398	0.199	1.014
0.167	0.408	1.030

Table IIB shows the effect of nitric acid on the potential for the same iridium concentration but a greater concentration of bromide ions. It will be noticed that the bromide ion concentration is still insufficient to permit reduction.

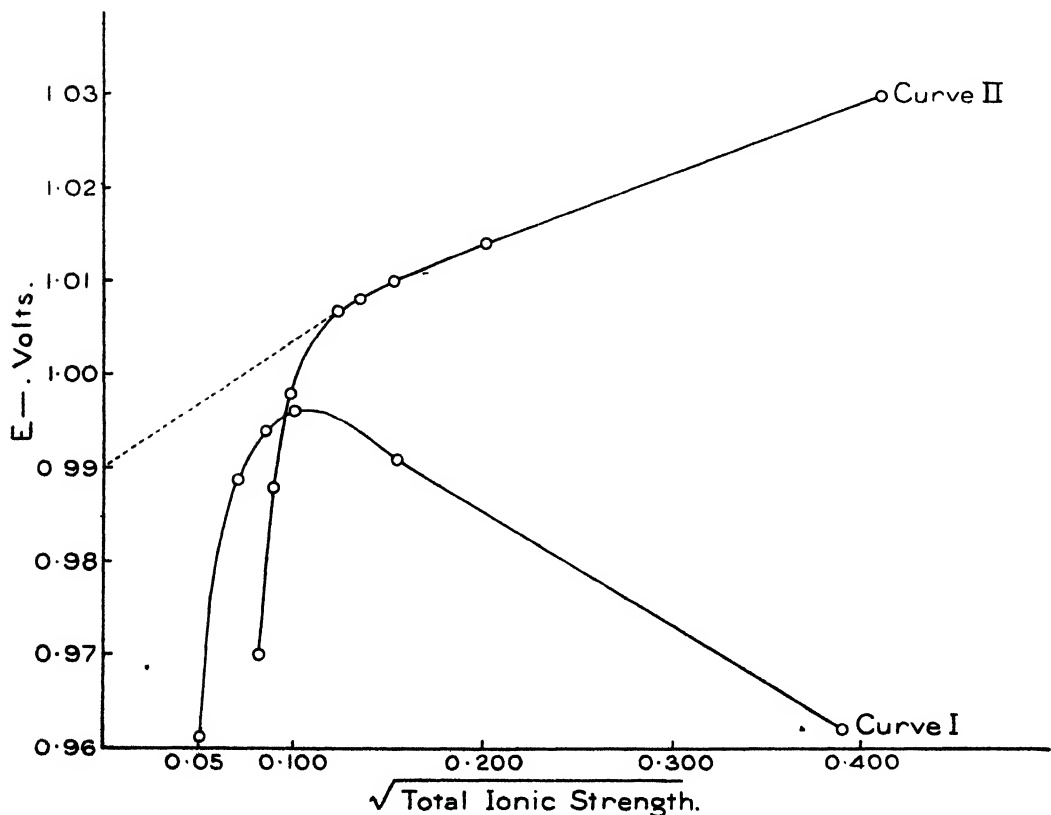
In the third series (Table III) the iridium concentration was maintained at the same value, nitric acid was added in sufficient constant amount to prevent

TABLE IIB.

Iridium Concentration Constant ($I=0.0060$), Bromide Ion Concentration Constant ($I=0.0023$), Nitric Acid Concentration Varied.

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0083	0.0906	0.983
0.0115	0.107	0.999
0.0150	0.122	1.002
0.0183	0.135	1.012
0.0248	0.153	1.010
0.0285	0.168	1.012
0.0332	0.182	1.013
0.0415	0.203	1.014

Curves I, II



hydrolysis, and the ionic strength raised with potassium bromide. The potential fell away sharply owing to reduction of the bromiridate and loss of bromine.

TABLE III.

Iridium Concentration Constant ($I=0.0060$), Bromide Ion Concentration Varied, Nitric Acid Concentration Constant ($I=0.0100$).

Total Ionic Strength.	$\sqrt{\text{Total Ionic Strength.}}$	Potential.
0.0165	0.129	1.008
0.0265	0.163	1.004
0.0332	0.183	0.993

SUMMARY.

The oxidation reduction potential of the bromiridate-bromiridite system at infinite dilution was found to be 0.99 volt at 20° C. The system behaved as a typical anionic system, but a unique feature was the reduction of the oxidant by bromide ion as the ionic strength was raised.

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THE GEOLOGY OF THE STANHOPE DISTRICT, N.S.W.

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With Plate V and three text-figures.

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INTRODUCTION.

The Stanhope District is situated on the northern side of the Hunter River about eight miles north of Branxton and about 140 miles from Sydney.

The area studied is of approximately 50 square miles, bounded to the east by Lamb's Valley Road, to the west by the Hunter overthrust fault, to the south by the Hunter River, and to the north by the Webber's Creek fault.

Walkom (1913) published a paper on the geology of the Glendon Brook District in which the geology of the Cranky Corner Basin and a general survey of the geology surrounding the basin is given. However, Osborne (1926) examined in detail and published the geology of a portion of this area, the Mirannie and Mt. Dyrning District, which lay to the north-west of the Stanhope District and is bounded by the Webber's Creek fault. The general geology of the Gosforth District which links up with that of the Stanhope District along Lamb's Valley Road to as far north as the bridge across Lamb's Creek was published by Browne (1926). Osborne (1927) published the geology of the area between Paterson and Lamb's Valley which links up with that of the Stanhope and Gosforth Districts to the north.

The Stanhope District affords the geologist with representatives of both the Volcanic and Glacial Stages of the Kuttung as well as most stages of the Permian, which, with the exception of those of the Cranky Corner Basin, have been faulted against the Kuttung rocks. The district also yields its share of the great structural pattern of the Hunter River District.

PHYSIOGRAPHY.

The Stanhope District is only a small area in a larger physiographic unit, the Hunter River District. The topography of the Hunter River District has an aspect of late maturity and is the result of stream action upon a peneplain which was elevated, with a tilt to the south, to a plateau during the Kosciusko uplift at the close of Tertiary time. Browne (1926) regards the peneplain before uplift as probably being continuous with the Hawkesbury sandstone country of the Broken Back Range and other high land to the south and south-west. In all probability the Hunter River District matured at an early stage as a result of the unresistant nature of the soft Permian strata and old fault planes in the Kuttung strata through which the river flows.

Viewing the physiography of the Stanhope District from the rise on the southern bank of the Hunter River at a point midway between Lamb's Valley Road and Elderslie, the most noteworthy feature is the relationship of topography to the geological structure. To the north about $2\frac{1}{2}$ miles from the river there suddenly rises the southern edge of a dissected plateau, which extends from Lamb's Valley Road in the east, where it almost takes a right-angled bend to the north having been dissected by Lamb's Creek, and to Elderslie in the west, where it also takes a bend almost at right angles to the north. A few remnants, such as Tangorin, 1,554 feet, Durham Peak, 1,250 feet and Lamb's Mountain, 1,100 feet, form eminences on the plateau and indicate its height. This plateau is an excellent example of the relationship of the geology to the physiography. Its edge is a dip escarpment of toscanite, which in comparison with the softer underlying tuffs and tuffaceous conglomerates is more resistant to erosion. To the east the volcanic rocks, such as toscanite, pyroxene andesite and rhyolite, give rise to a series of hills, which appear as a succession of dip slopes and dip escarpments and trend in an east-west direction, while to the west the area examined is bounded by two rows of hills trending in a north-south direction, the one further west being the higher composed of conglomerate and felsite, the other composed of hornblende andesite.

In the foreground from the point of observation is gently undulating country, 50-300 feet high, bound on all sides by the higher land described above. This country for the most part consists of conglomerates, tuffs and thin bands of volcanic lavas. It has been dissected by small creeks.

The faulting, which has occurred in the area, has not given rise to fault scarps. This is probably due to the fact that faulting antedated the uplift of the peneplain. On the other hand the faults have played a considerable part in the determination of the physiography, for in most cases the faulting has resulted in the softer Permian rocks having been brought up against the harder Kuttung lavas. This is evident in the western portion of the district, where the Hunter overthrust fault has brought the Permian sediments up against the Kuttung conglomerates and lavas, the result being that the more resistant Kuttung rocks give rise to the row of hills trending north-south. East of this fault one sees the more or less rugged physiography of the Carboniferous rocks, while to the west of it the physiography is gently undulating.

The most important feature of the Hunter River physiography is the river itself. The part of it which flows through the area under examination is characterized by much meandering, indicating a very mature stream. Its course in some parts can be explained by the geological formations. For instance, in the Stanhope District, the river flows in an easterly direction, its course being determined by the Hunter overthrust fault. The flood plains on the northern side of the river are rather narrow but nevertheless it has built wider flood plains on the concave sides of the meanders and practically none on the convex sides.

Two levels of alluvium are present along the northern bank of the river. These river terraces are at heights of 100' and of 50' above the present day river

bed. They indicate subsequent minor uplifts, which have enabled the river to cut down through its former flood plains to a new base level. In parts, for example near Goodyear's, the river has completely eroded away the lower of the two terraces and has revealed good rock sections.

Three important tributaries of the Hunter River are Glendon Brook, Stanhope and Lamb's Creeks, all of which have a mature aspect in parts, being characterised by much meandering. Glendon Brook appears to have taken advantage of the Hunter overthrust and Webber's Creek faults. The valley of Lamb's Creek is impressive physiographically. It is a wide U-shaped valley, the particular shape being due to the hard thick capping of toscanite underlain by softer tuffs and conglomerate. To account for the wide valley the creek seems to represent a shrunken remnant of a very impressive stream, which probably existed in earlier times. Today all one sees is a narrow creek meandering along the middle of the wide valley floor.

Stanhope Creek, whilst revealing evidences of maturity in parts, has not carved out such an impressive valley. It has carved a rather narrow V-shaped valley through the toscanite before it enters the undulating country between the plateau and the Hunter River. Both the Stanhope and Lamb's Creeks show evidence of youth towards their sources in the plateau area. In this region intermittent waterfalls occur along their courses due to resistant bands of rock such as the toscanite.

All of the hills are characterised by talus slopes and it is through these slopes that numerous small consequent streams are cutting their beds. Along the edge of the Tangorin Range to the north and east and the Moonabung Plateau to the east of Lamb's Valley Road these streams are seen to occur at intervals of about 50 yards. In most cases these creeks are cutting across the strike of the beds and link up with one of the more important creeks. For example those from the Moonabung Plateau link up with Lamb's Creek and those from the Tangorin Plateau with Lamb's Creek in the east and with Stanhope and Dutton's Creeks in the south and Glendon Brook in the north. Quite often the creeks have taken advantage of minor faults and joint planes. Dutton's Creek is an example of this. Just before it joins the Hunter River it has taken advantage of the weakness along the Hunter overthrust fault. The creek running beside the Cranky Corner Road has carved out a deep valley through hard rhyolite, conglomerate and toscanite.

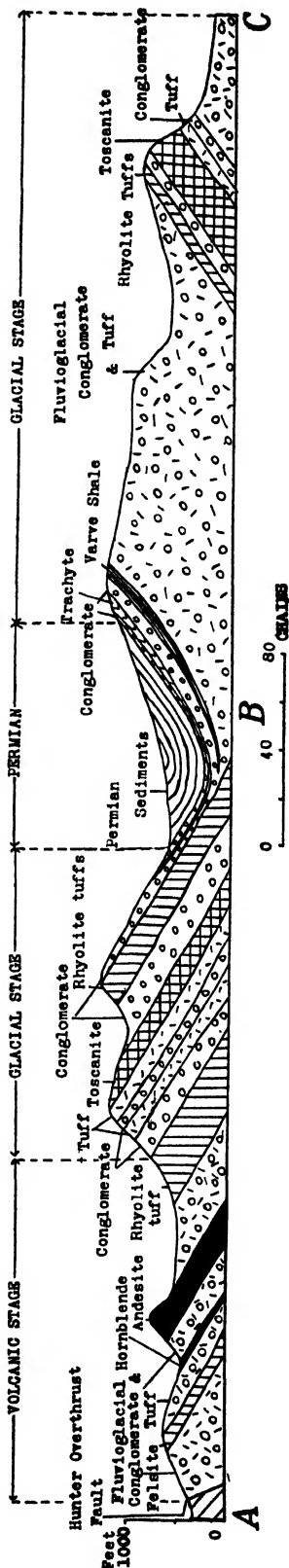


Fig. 1.—General Geological Section across Stanhope Area. (Line A-B-C on map).

Evidences of numerous slickensides in the rocks along Cranky Corner Road indicate instability even though there is no evidence of a fault.

STRATIGRAPHY.

Carboniferous.

The Carboniferous rocks in New South Wales may be divided into two main divisions, namely the Burindi which consists of the marine beds, and the Kuttung which consists of terrestrial beds, these being glacial and volcanic for the most part. In the Stanhope District rocks of the Burindi Division are entirely absent but both glacial and volcanic beds of the Kuttung are well represented.

Osborne (1922) has divided the Kuttung rocks into (a) Basal Stage, (b) Volcanic Stage, and (c) Glacial Stage. In the district studied no example of the Basal Stage type has been found, but it appears as though the Volcanic Stage is equivalent to the combined Basal and Volcanic Stages of Osborne. See Figures 1 and 2.

Volcanic Stage. In the Stanhope District rocks of the Volcanic Stage are very well developed. All the series determined by Browne in the adjacent Gosforth District have been recognised. The volcanic series extends westwards for about seven miles in an unbroken arc from Lamb's Valley in the east to Elderslie in the west, where they swing to the north to Glendonbrook. At Elderslie they are cut along the strike by the Hunter overthrust fault, which extends northwards and across the strike at Glendonbrook by the Webber's Creek fault.

The series consists of the following flows :

	Feet.
Dacite tuffs and ignimbrites (including dacitic pitchstone)	800
Toscanite	260
Toscanite	400
Hornblende andesite (and hornblende andesitic pitchstone)	900
Pyroxene andesite (and pyroxene andesitic pitchstone)	1,200
Hornblende andesite (and hornblende andesitic pitchstone)	130
Felsite	160
Felsite	130
Pyroxene andesite	50
Pyroxene andesitic pitchstone	—
Rhyolite	920
Pyroxene andesite (and pyroxene andesitic pitchstone)	660
Rhyolite (faulted along strike)	—
Total	5,610

Each of these flows is separated over the greater part of the area by varying thicknesses of fluvio-glacial conglomerate and interbedded tuff. An average section through the Volcanic Stage is approximately 5,400 feet in thickness.

The lowest flow of the Volcanic Stage represented in the Stanhope District is seen outcropping along the northern bank of the Hunter River at the base of John's Hill and near Miss Bendeich's house. It is a very light coloured felsitic type of rock consisting of tiny phenocrysts of quartz and biotite. Its thickness cannot be ascertained as the flow has been dislocated along its outcrop by the Hunter overthrust fault which has also caused the rhyolite to be turned up steeply.

Immediately overlying this rhyolite is the lower flow of pyroxene andesite which resembles that of the upper flow described below. It is underlain by a thin flow of pitchstone.

The next flow is more or less the lowest rhyolite flow of importance. This rhyolite is very persistent and outcrops from Lamb's Valley Road along both sides of the Stanhope Road, crosses the road in front of H. Bendeich's property and continues east-west until it is cut out by the Hunter overthrust fault near Dutton's Creek. John's Hill between Stanhope Road and the Hunter River is composed of this rhyolite, which has given rise to a dip slope to the north and a dip scarp to the south. The rhyolite varies in character throughout the flow. At Lamb's Valley the rock is pinkish brown in colour, exhibiting excellent flow structure on a relatively large scale and containing veins of chalcedony. In places where the flow structure is not so predominant the phenocrysts are more distinct and appear to be lath-shaped crystals of orthoclase. The rock contains fragmentary inclusions. Behind W. Bendeich's house the rock is a brownish andesitic type containing small phenocrysts of plagioclase. There is also underlying this phase in the same area a light pink coloured rock which seems to resemble a weathered phase of the Lamb's Valley type. At the back of Harrigan's the next phase occurs. This consists of phenocrysts of orthoclase and abundant glassy quartz in a dark brown coloured stony groundmass. West of John's Hill the rhyolite is separated by a thin band of tuff and conglomerate. The felsite above the sedimentary rocks is lighter coloured, having a bluish grey matrix, fawn when weathered, with larger phenocrysts of pink orthoclase. It also contains fragments of foreign material.

Between this and the next felsite is a very thin flow of pyroxene andesite which in places is considerably deuterically altered. It only outcrops intermittently in an east-west direction from near Lamb's Valley to Stanhope Creek.

Overlying the John's Hill rhyolite at Lamb's Valley is a lenticular outcrop of pyroxene andesitic pitchstone which forms a hill on the eastern side of Lamb's Valley Road.

Two fairly thin flows of felsite come next in ascending order in the Volcanic Stage. These vary in character and like all the other lavas contain fragmental inclusions. In Dutton's Creek is a phase of the upper flow almost identical with the pink coloured phase containing biotite of the top dacite tuff series.

A thin lower flow of hornblende andesite lies below a thick flow of pyroxene andesite, separated from it by a band of tuff and conglomerate. It is very similar in character to the upper flow described below. It is probably the equivalent of the Martin's Creek type. It is not as persistent in outcropping and disappears to the east just after the upper pyroxene andesite is met. Whether this hornblende andesite continues under the talus from the hills it is impossible to say. Like the upper flow, it too is deuterically altered, and in places it is difficult to recognise the deuterically altered rock as hornblende andesite. When it is a dark reddish brown in colour and the hornblende phenocrysts are almost microscopic it closely resembles some of the earlier felsites. This flow is underlain by a thin flow of hornblende andesitic pitchstone.

The highest ridge of the series of hills to the east of the district is composed of pyroxene andesite. This is the upper flow of pyroxene andesite and has a maximum thickness of about 1,200 feet. The upper part of the flow is glassy and in all probability is a separate flow overlying the lithoidal phase. It is impossible to map a boundary between the two phases. Outcrops of the flow are terminated in portion 104, Parish of Stanhope, by a small hill of pitchstone. The lithoidal phase when fresh is a dark grey in colour and is fairly coarse grained in comparison with the other andesites. The sudden termination of such a thick flow seems strange and may indicate a possible fault but this cannot be so as other beds are continuous. The other solution is that it probably thins out rather quickly towards the west under some high level gravels from Stanhope Creek.

The hornblende andesite overlying the pyroxene andesite also forms part of the hills to the east and in parts it is difficult to distinguish between it and the overlying toscanite, especially when the hornblende andesite contains free quartz. This flow of andesite is fairly thick and is wonderfully persistent. It extends right across the area, turning to the north at Elderslie, where it is faulted by minor tear faults associated with the Hunter overthrust fault. When fresh the hornblende andesite is a bluish black colour with bright glassy phenocrysts of plagioclase and black phenocrysts of hornblende and biotite. The andesite varies in character, for in places it contains an abundance of quartz and would then more suitably be termed a dacite. In places along the flow the andesite has been deuterically altered. Where this has happened the groundmass becomes lighter in colour, often changed to a grey colour, and the plagioclase phenocrysts become whiter. Where the rock is weathered the groundmass is very light, the felspar white and the hornblende has taken on a dull greenish black appearance due to alteration to chlorite. Even in hand specimens one can see the phenocrysts of plagioclase altered to chlorite at the centre. The rock contains inclusions, the amount varying in different parts of the flow. Both this and the lower hornblende andesite flow are parted in a peculiar fashion which gives rise to rather thin blocks resembling flagstones. It is a noticeable fact, however, that where free quartz is fairly abundant the hornblende andesite does not bear this particular type of parting. The acid phase seems to be towards the base of the flow. A glassy phase of the hornblende andesite occurs in places below the lithoidal phase. This pitchstone phase and all the other glassy phases of the andesites are characterised by veins through the rock of red limonite which forms ridges on the weathered surfaces.

Overlying the two flows of the hornblende andesite are thin flows of an andesite rock, probably a keratophyre, which consists of numerous lath-shaped phenocrysts of white plagioclase in a dark purplish coloured groundmass. It appears to weather very easily. The flow above the upper hornblende andesite is more persistent than the one above the lower.

Overlying the hornblende andesite is a flow of toscanite which consists of two horizons separated by a thin band of conglomerate. The toscanite gives rise to the most northern row of hills which extend west from Lamb's Valley. Both horizons disappear about portion 104, Parish of Stanhope, the only trace of the toscanite found elsewhere being along the southern boundary of the top lava flow in the Volcanic Stage further west and at Glendonbrook. The toscanite of each horizon differs slightly, that of the upper horizon being a brownish colour and containing abundant quartz and plagioclase phenocrysts with a little orthoclase and biotite, while that of the lower horizon is a khaki colour, being slightly weathered and containing phenocrysts of quartz and plagioclase. Both are usually streaked with veins of limonite and contain fragmental inclusions.

The topmost bed in the Volcanic Stage consists of a series of "flows" of dacitic pitchstone, dacite tuff and ignimbrites (Marshall, 1935) which outcrop from Lamb's Valley Road across the Stanhope District to Elderslie, where they swing to the north and continue to outcrop to Glendonbrook, where they are cut by the Webber's Creek fault. The total maximum thickness is about 800 feet and is reached near Lamb's Valley Road, where most phases appear to be present. There appears to be at least five phases. The phase at the base is ignimbritic and is not persistent throughout the length of the outcrop but good outcrops occur above the toscanite. Overlying the ignimbrites is a thin flow of dacitic pitchstone which contains a fair abundance of biotite and inclusions of fragments of older lavas. This pitchstone outcrops in a small quarry along Lamb's Valley Road, and near Tangorin. In places it appears to be transgressive into the overlying light pink coloured rock, rich in veins of chalcodony

which appear to be elongated in the direction of flow. Along Stanhope Creek the black dacitic pitchstone is absent, but overlying the basal ignimbrite is a pink rock, different from the rock just mentioned, containing numerous fragments. On microscopic investigation this rock type appears to be a dacite tuff and is probably the fragmental equivalent of the pitchstone. Good outcrops of this rock also occur along Dutton's Creek. The next phase is that which overlies the pitchstone. It is a light coloured rock, white in some places, pink in others. This type is very rich in biotite phenocrysts and contains a few tiny quartz phenocrysts and abundant fragmental remains. It appears to be the devitrified equivalent of the pitchstone. Above this phase is a light fawn coloured rock, probably an ignimbrite, containing abundant fragments and phenocrysts of felspar. It forms a persistent outcrop towards Glendonbrook. The ignimbrite of the topmost phase has a brownish red coloured groundmass and contains abundant white phenocrysts of plagioclase and some biotite. It also contains fragments of other rocks which have become elongated in the direction of flow. This phase outcrops intermittently along the whole length of the flow.

To the west of the eastern portion of portion 104, Parish of Stanhope, the lava flows are separated by bands of varying thicknesses of tuff and conglomerate. In the creek banks good sections of conglomerate can be seen. In all cases the boulders vary in size from a fraction of an inch to about eight feet in diameter. They are all waterworn but no ice scratched pebbles have been found. These boulders are so large and so irregularly sorted and dumped, some being on end, that it seems that they must have been deposited by glacial action. In most cases the matrix is tuffaceous and has weathered rather readily, leaving the boulders irregularly sorted and scattered over the surface. Near Hardes' house the fluvio-glacial conglomerate underlying the lower hornblende andesite has a hard tillitic matrix.

The boulders and pebbles vary in composition. For the most part they consist of underlying lavas, cherts, quartzites, aplites and pink granite. The fluvio-glacial conglomerate between the two hornblende andesites which outcrops along the bank of the Hunter River contains numerous boulders of all sizes of hornblende andesite which are held together by what appears to be a very coarse tuffaceous matrix. The matrix is very decomposed.

The tuff varies in texture from fine grained to fairly coarse grained. It is generally pink in colour and consists of fragments of all kinds. It is easily eroded and in the beds and banks of creeks has a curved waterworn appearance. For the most part the tuff is feldspathic. Mostly in the Volcanic Stage the tuffs and conglomerates are interbedded and the beds are usually so thin that it is impossible to indicate them on a map or section. They often appear to merge into each other and one gets gradations such as a pebbly tuff and a tuffaceous conglomerate. A peculiar type of conglomerate occurs between the lithoidal pyroxene andesite and the small lenticular outcrop of pyroxene andesitic pitchstone at Lamb's Valley. It is well exposed in a creek on the opposite side of the road to the Post Office. It consists of pebbles of pyroxene andesite and of cherty material set in a matrix of pyroxene andesite. It is probable that an earlier flow of pyroxene andesite had time to consolidate, became disrupted and rounded by water action before another flow, probably from the same fissure, flowed over the water-worn pebbles and caught them up. This pyroxene andesite conglomerate does not continue on the western side of Lamb's Valley Road, its place being taken by the ordinary fluvio-glacial conglomerate so characteristic of the district.

Glacial Stage. The Glacial Stage of the Kuttung rocks is divided into two sub-stages, namely the Lower Glacial Stage and the Upper Glacial Stage, which are separated by a thick flow of toscanite. The Upper Glacial Stage constitutes

the main glacial beds in the district. A general section through the Glacial Stage reveals the following succession :

	Feet
Conglomerate	50
Trachyte flows	100
Varve shales	150
Conglomerate	100
Tuff with <i>Rhacopteris</i>	100
Conglomerate	870
Rhyolite tuff	530
Conglomerate, varves, tillite	530
Toscanite	530
Conglomerate	
Tuff	1,320
Conglomerate	
Total	4,280

Vulcanicity did not cease at the end of the Volcanic Stage as evidenced by the toscanite and rhyolite tuff and the tuffaceous nature of some of the sediments.

The basal bed of the Glacial Stage is one of fluvio-glacial conglomerate consisting of large water-worn boulders of older lavas, pink granite, aplite, quartzite and chert. To the east at Lamb's Valley the conglomerate is characterised by large rounded boulders of grey granite and attains a thickness of about 750 feet. Good outcrops are exposed along Lamb's Creek near the bridge across the road and to the north along either side of Lamb's Valley Road. The most westerly position where the grey granite conglomerate outcrops is along the bank of Sandy Water Holes. Here the grey granite boulders are less numerous, while the boulders of pink granite, aplite and lavas increase in number. At Lamb's Valley the large boulders of the grey granite predominate over a few smaller pebbles of chert, aplite and pink granite. The matrix appears to be fairly coarsely tuffaceous and weathers rather readily. This basal conglomerate is probably the equivalent of the coarse conglomerate which occurs at the base of the Glacial Stage in the Paterson-Clarencetown area.

Overlying this basal conglomerate is a thick bed of pink tuff which for the most part is fine grained and micaceous. It resembles the tuffs of the Volcanic Stage. Interbedded with the tuff is a thin band of cherty tuffaceous rock containing *Rhacopteris*. The pink tuff in places passes into a brownish coloured sandy tuff. Towards the top of the bed the tuff becomes pebbly and passes into a conglomerate.

Above the conglomerate is a thick band of toscanite which has given rise to the steeply sloped range of mountains extending across the district. It is very persistent and resistant to erosion.

Along the Cranky Corner Road one is able to see most of the succession of the beds in the Upper Glacial Stage above the toscanite. Following the toscanite is a thin flow of felsite consisting of phenocrysts of quartz, plagioclase and some biotite in a fawn coloured groundmass. This felsite can be seen on Durham Peak, where it has a slightly different appearance. Here it is a pale pink and green rock with phenocrysts of quartz and orthoclase and has been kaolinized to a certain extent.

Following this felsite are two thin beds of varve shales which are separated by about 25 feet of tillite, tuff and fluvio-glacial conglomerate. The varves are a chocolate brown colour and are easily weathered as indicated by the small

fragments strewn along the road. The upper band is of the fine sandy type called by Browne "varvoids". Along a tributary creek to Stanhope Creek the "varvoids" are sandier, less weathered, well banded and show contortions in places. It is possible that these are not true varves but are fine banded tuffs and the contortions are due to slumping. To the west near Sandy Water Holes the varves are not seen, but the felsite is overlain by a thick bed of fluvio-glacial conglomerate which contains abundant fossil wood. This conglomerate gives rise to the steep sides of the valley of Sandy Water Holes.

Another thin band of tillite follows, succeeded by a thin bed of rhyolite tuff which is generally pink in colour. This tuff passes into a coarser tuff and then to a green siliceous tuff. Overlying these tuffs is a thick bed of rhyolite tuff which seems to attain its maximum thickness of 700 feet near Cranky Corner. It varies considerably in character, and generally speaking consists of phenocrysts of quartz, both feldspars and biotite in a groundmass which for the most part is kaolinized and varies in colour. Towards the top of the bed the rock becomes megascopically tuffaceous and then passes into a very coarse rhyolite tuff which contains angular fragments of rhyolite, chert and quartz up to about half an inch in width. In comparison with the number of fragments, there appears to be very little matrix. The rhyolite tuff appears to peter out quickly to the west.

The rhyolite tuff passes into a fluvio-glacial conglomerate and then a pebbly tuff. Overlying the conglomerate and tuff is a thin band of tillite. It is light in colour and contains angular fragments in a very hard tillitic matrix. It outcrops along the Cranky Corner Road at Cranky Corner. The conglomerate at Cranky Corner immediately below the tillite contains both rounded and angular fragments which include a fair quantity of varve shales. As no similar varves have been found in the district below this conglomerate, the fragments probably came from further east, where they do occur on a lower horizon.

Next comes a persistent band of cream-coloured varve shales with a maximum thickness of about 150 feet, which in places are contorted. It is overlain by a few feet of fluvio-glacial conglomerate and tillite. The varves thin out quickly in the direction of Cranky Corner. East of Cranky Corner they are underlain by a few feet of conglomerate and then a band of light coloured tuffaceous sandstone which has interbedded with it a very fine white tuffaceous shale containing abundant remains of *Rhacopteris*. This band of tuff continues in a north-easterly direction and is found to contain marine fossils which include *Spirifer striata* (?), *Dielasma* and *Schizodus* and remains of plant stems which are indeterminate.

The tuff appears to thin out towards and disappears at Cranky Corner. However, another tuff which seems to be on the same horizon occurs but contains no fossils. This tuff may be the terrestrial equivalent of the marine tuff. The conglomerate between the tuff and varve shales is fluvio-glacial, and towards the east becomes thicker and more tuffaceous. In parts it is actually a pebbly tuff.

To the east of Cranky Corner is a very thin flow of toscanite which resembles the Paterson type. It is interbedded with the tuffaceous conglomerate between two thin bands of varve-like rock.

Towards the top of the Carboniferous in the district near Cranky Corner and trending north-west and north-east is a thin flow of trachyte which appears to thicken towards the north-east, where it is found associated with a trachyte breccia. There appears to be about three flows of the trachyte as in places the trachyte is interbedded with conglomerate and tillite above the varves as at Cranky Corner and further east with the varve shales, which it seems to have hardened. Of the three flows the lowest is porphyritic, the middle fine grained trachyte, and the top flow amygdaloidal. The fresh specimens are dark grey in colour but weather to a brown rock. The very weathered specimens of the

amygdaloidal type are khaki in colour and the amygdules have either been stained or replaced by brown limonite.

Permian.

The rocks of Permian age were not studied in detail but the following are a few facts noted.

The most important outcrop of Permian rocks in the district is that which occupies the Cranky Corner Basin. Only the beds at the base of the series were noted. The rocks belong to the Lower Marine Series.

The basal bed is very persistent and consists of tuff which weathers to a bluish grey coloured rock. Along the eastern boundary of the Permian the tuff passes into a rather felspathic type. It is a dark grey in colour and contains abundant orthoclase and plagioclase crystals. Marine fossils are found in this tuff and include *Spirifer*, *Martiniopsis*, *Ptychomphalina morrisii* and *Nuculana*.

The next band appears to be the *Eurydesma cordata* horizon. This is a persistent horizon and can be traced along the south-eastern portion of the basin. The bed is a conglomerate and contains countless numbers of *Eurydesma cordata* and some large *Pectens*.

Another outcrop of Permian beds, probably Lower Marine in age, is on the southern side of the Hunter overthrust fault. The series here consists of a band of tuffaceous sandstone containing remains of *Fenestella* and *Ptychomphalina morrisii*.

The Upper Coal Measures are represented along the western side of the Hunter overthrust fault. Some of this series outcrops along the river and for a short distance along the Elderslie Road.

The Permian and Carboniferous strata in the Stanhope District appear to be conformable in spite of the fact that there was a transition from terrestrial to marine sedimentation at the end of Carboniferous time.

Pleistocene and Recent.

Pleistocene deposits in the Stanhope District are represented by the high level alluvium of the terraces along the Hunter River. These terraces are 100' and 50' above sea level and are regarded as being of Pleistocene age from the occurrence of *Nototherium* remains in them at Elderslie, recorded by Professor David (1907). They consist of alluvium and some pebbly material. At times it is difficult to distinguish between the high level gravel and the loose pebbles from the Kuttung conglomerates, as both contain similar types. The distinguishing feature is that the high level alluvium contains pebbles of red jasper which are not found in the conglomerate. These jasper pebbles have a peculiar weathering effect on the surface, such as small circular cuts. Only remnants of the high level gravels remain in places.

Recent deposits are represented by a cemented rubble which occurs irregularly distributed throughout the area. It consists of pebbles of all types of composition, some of which are rounded, others angular of all sizes cemented into a more or less compact mass which usually has a dirty grey colour. The matrix is porous and crumbly. This recent type of conglomerate is usually level bedded and lies unconformably upon the underlying rocks. Browne (1926) has described occurrences of similar deposits in the Gosforth and Pokolbin districts, and Osborne (1922) in the Paterson-Clarencetown area.

Recent deposits of alluvium in the form of fine sandy silt are to be found on the flood plains on either side of the Hunter River and along some of the creeks.

STANHOPE GOSFORTH-MOONABUNG SEAHAM-CLARENCETOWN

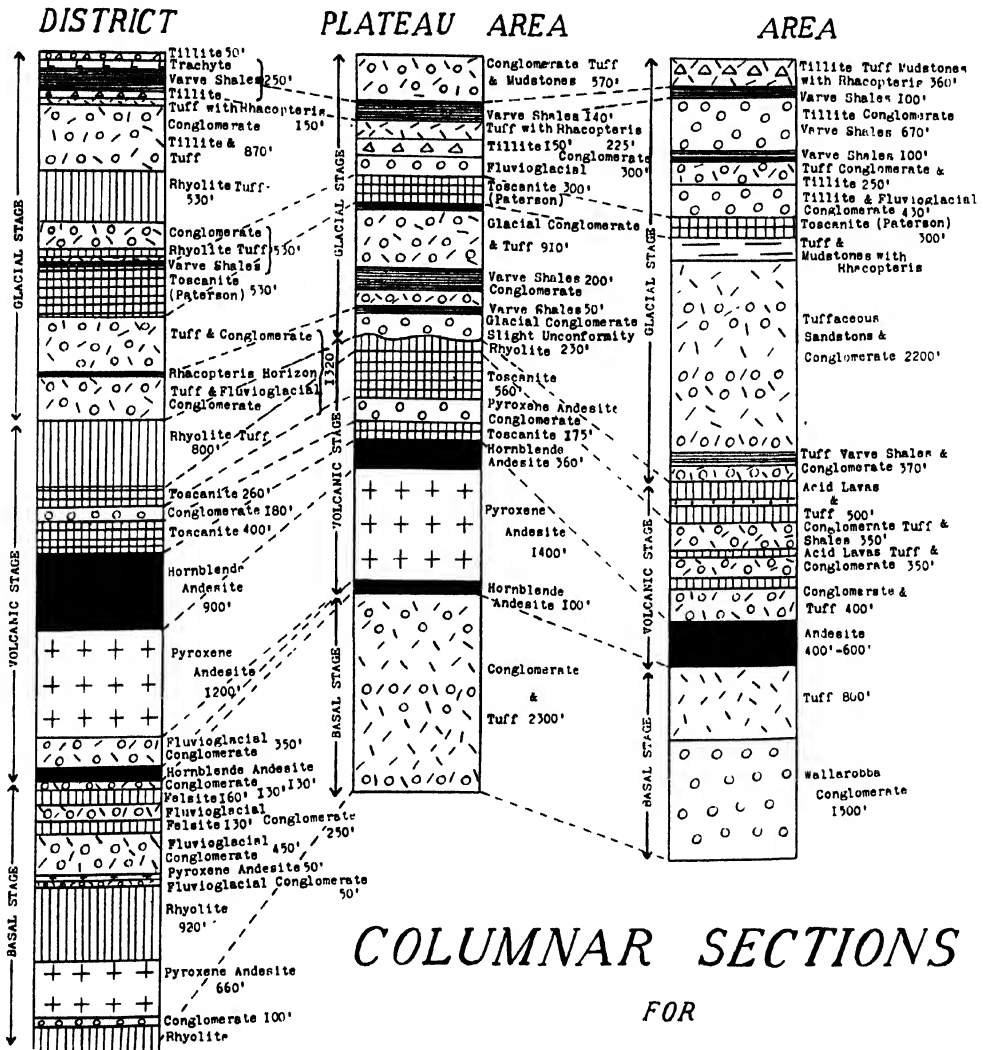


Fig. 2.

Correlation of Stratigraphy with that of Adjoining Areas.

The two areas used in the correlation of the stratigraphy of the Stanhope District are the Gosforth-Moonabung Plateau area which adjoins it and the type area, the Seaham-Clarencetown area further to the east.

The stratigraphy of the adjoining area corresponds very well with that of the Stanhope District, while that of the Seaham-Clarencetown area corresponds only to a certain extent.

As in the Seaham-Clarencetown area the stratigraphy of the other two areas has been divided as well as possible into the three stages, namely Basal, Volcanic and Glacial. The Martin's Creek hornblende andesite horizon present in the three areas is taken as the base of the Volcanic Stage and the acid lava flow, commonly called a rhyolite, as the top of the stage. The Glacial Stage can be divided in all areas by the Paterson toscanite into the Upper and Lower Glacial Stages.

The Basal Stage of all three areas does not correspond. In the Stanhope District the Basal Stage is represented by a series of lavas separated by fluvio-glacial conglomerates and tuff as in the Volcanic Stage, into which it passes without any change. The Basal Stage in the Gosforth-Moonabung plateau area is represented by a great thickness of tuff and conglomerate and so differs from that of the Stanhope District and also from the Seaham-Clarencetown area, where the base of the Kuttung is represented by a great thickness of conglomerate, the Wallarobba conglomerate, and tuff which contains *Lepidodendron*.

The Volcanic Stage in all three areas compares exceptionally well, particularly the Gosforth-Moonabung Plateau and Stanhope areas. The lava flows seem to attain their maximum thickness in the Stanhope District.

The Glacial Stage was ushered in with a band of fluvio-glacial conglomerate, followed by a series of tuffs which in the Gosforth-Moonabung Plateau and Seaham-Clarencetown areas contain thin bands of varve shales. In the Gosforth-Moonabung Plateau area there is a slight unconformity between the Volcanic and Glacial Stages. The Upper Glacial Stage is represented throughout by a series of fluvio-glacial conglomerates, tillites, varves and tuffs, but in the Stanhope District there has been a greater continuation of volcanic activity which is not represented in the other two districts. This volcanic activity is represented by flows of rhyolite and trachyte. Another feature of the Stanhope District is the presence of a thin band of tuff containing marine fossils.

To summarize, the Stanhope District cannot be satisfactorily divided into the Basal, Volcanic and Glacial Stages and proves that the boundaries between the stages are only arbitrary and only hold for the type area. The stages can only be gained when considering the time factor and indicate that the area was undergoing different conditions at the same time that the other areas were experiencing other conditions, as is expected in a volcanic area. For instance, in the Stanhope District both volcanic and glacial conditions were prevalent throughout the whole of Kuttung times as represented by the lava flows and the fluvio-glacial conglomerates, tillites and varve shales. The type area, however, can in contrast be satisfactorily divided into the three stages as three different types of conditions prevailed. In the Gosforth-Moonabung Plateau area the divisions hold to a certain extent. Here volcanic activity commenced at a later stage than in the Stanhope District and at an earlier stage than in the type area, as the Basal Stage contains a greater thickness of tuffs and towards the top, a flow of felsite.

PETROLOGY.

Petrography.

The petrography of the rocks in the Stanhope District is very similar to that of most of the rocks of the Kuttung from other districts. The rocks vary from

basic intermediate volcanic to acid volcanic and are of numerous types. The three main groups are the andesites, toscanites and rhyolites, which vary within themselves with regard to the percentages of the various mineral constituents.

Petrological problems such as deuteric action involving albitization, chloritization and kaolinization, and devitrification with its allied structures present themselves.

ANDESITES.

The andesites consist of two distinct groups characterized by hornblende and biotite on one hand and augite and hypersthene on the other. Both groups comprise lithoidal and glassy phases.

Pyroxene Andesites.

Glassy Varieties. Megascopically the pyroxene andesitic pitchstones resemble very much the hornblende type described below, with the exception that the pyroxene type contains more plagioclase phenocrysts, which are a creamy colour.

Microscopic investigation reveals that the tabular crystals of plagioclase are the most abundant phenocrysts developed porphyritically in the rock. They are idiomorphic in form and appear quite fresh. The approximate compositions are as follows. The plagioclase of the pitchstone underlying the lowest flow of pyroxene andesite is $Ab_{56}An_{44}$, that from the lenticular shaped outcrop at Lamb's Valley $Ab_{52}An_{48}$, while that of the pitchstone overlying the main pyroxene andesite flow is $Ab_{56}An_{44}$. Pseudo inclusions of groundmass are present in some crystals, also small augite inclusions.

Other phenocrysts of importance are the pyroxenes, augite and hypersthene. These have developed in a subidiomorphic prismatic form. Some of the augite shows simple twinning. The hypersthene shows fairly strong pleochroism and good cleavage. It is slightly greater in amount than the augite.

Hornblende phenocrysts are present only in the pitchstone under the lowest pyroxene andesite, and then they are greater in amount than the pyroxenes. These phenocrysts are subidiomorphic and are of the brown variety.

Magnetite is abundant as inclusions in the plagioclase and pyroxenes as well as in the groundmass.

Apatite crystals vary in size and are present in some of the plagioclase and pyroxene.

The groundmass is light brown in colour and consists wholly of glass. There is evidence of resorption in all the phenocrysts. In the pitchstone associated with the main pyroxene andesite the groundmass shows signs of devitrification, having tiny crystals of felspar in the glass.

Lithoidal Varieties. In the district there are three separate flows of the lithoidal variety. Specimens from these flows differ slightly megascopically. In parts of the lowest flow the andesite resembles that of the upper, whereas in others it appears to have a bright dark groundmass in which the phenocrysts of plagioclase are colourless and do not show up against the groundmass. When altered the rock is a dark brownish colour. The andesite of the second flow varies in character and for the most part is deuterically altered to a greyish colour. The upper flow consists of fairly large phenocrysts of white plagioclase in a dark grey groundmass with smaller phenocrysts of augite.

Microscopically all the lithoidal types are somewhat similar. They consist of abundant phenocrysts of plagioclase and a smaller quantity of pyroxene in a light coloured groundmass.

The plagioclase is in idiomorphic tabular crystals and is andesine $Ab_{59}An_{41}$ in the lowest flow and labradorite $Ab_{46}An_{54}$ in the upper flow. The plagioclase

in the middle flow is completely albitized. It shows zoning by composition, decomposition and inclusions. Twinning according to the albite law is very strongly developed and in some cases both albite and Carlsbad types occur together. Usually the plagioclase is partly decomposed to kaolin and partly deuterically altered to albite, but not as much as in the case of the hornblende andesites. In some cases the plagioclase is altered to chlorite towards the centre. The chlorite in turn is replaced by iron ore. For the most part the inclusions are magnetite, pyroxene and some apatite.

The pyroxene includes both augite and hypersthene in variable amounts, but together are subordinate in amount to the plagioclase. In the lowest flow augite is greater than hypersthene and in the middle and highest flows hypersthene is greater than augite. They form subidiomorphic prismatic crystals. The hypersthene shows rather good pleochroism and cleavage. The augite, on the other hand, is non-pleochroic and often shows good simple twinning. The pyroxene on the whole is rather fresh, only being altered around the edges to a dark brownish green mineral which is probably chlorite. Abundant inclusions of magnetite and apatite are present.

Idiomorphic phenocrysts of hornblende occur in the lowest flow. This hornblende is partly chloritized and in parts seems to have been resorbed to some extent by the groundmass.

Magnetite is abundant in the andesites appearing as phenocrysts and as tiny grains scattered throughout the groundmass, particularly in the lowest flow.

Apatite is found as inclusions and in the groundmass. It is usually idiomorphic in form.

The groundmass is generally cryptocrystalline and does not show any glassy patches. Under high power the groundmass appears to be felspathic and contains patches of green chloritic material which is probably pseudomorphic after some mineral.

Hornblende Andesites.

Glassy Varieties. Megascopically the pitchstone or glassy phases of the hornblende andesites are black rocks with a bright resinous lustre streaked with veins of red hæmatite and limonite. They contain phenocrysts of glassy plagioclase, hornblende and biotite. The pitchstone is very brittle.

Microscopically the rock is porphyritic and consists of phenocrysts of plagioclase, quartz, hornblende, pyroxene including both augite and hypersthene, and biotite in a glassy groundmass. Accessory minerals are magnetite and apatite.

The plagioclase makes up about 60% of the phenocrysts and is andesine $Ab_{68}An_{32}$. It is in the form of subidiomorphic tabular crystals which for the most part are clear and exhibit cracking in two directions. The crystals show slight resorption effects around the edges and in some cases contain pseudo inclusions of the groundmass. Zoning by composition and albite twinning are well exemplified. Inclusions include pyroxene, magnetite and apatite.

Quartz phenocrysts are relatively abundant but are subordinate in amount to plagioclase. They are subidiomorphic and show resorption effects. They show cracking, as does the plagioclase.

The pyroxenes are augite and hypersthene and have crystallized in subidiomorphic prismatic form. They exhibit good cleavage and fracture. Hypersthene is greater in amount than augite.

The hornblende is in subidiomorphic prismatic form and is quite subordinate in amount to plagioclase and is also less abundant than the pyroxenes. It is of the brown variety and shows strong pleochroism.

Biotite is in a very small quantity and is brown, showing very strong pleochroism. It is prismatic in habit.

Magnetite is rather abundant and is found both as inclusions in the phenocrysts and in the groundmass. The crystals are cubic and some show resorption effects.

Apatite is in a small quantity and occurs both as inclusions and in the groundmass. Small basal sections are common, as well as tiny prismatic crystals.

The groundmass is very pale brown in colour and is wholly glassy. In it can be recognized tiny as well as the large phenocrysts of the types mentioned above. It shows flow structure and is streaked in parts by narrow bands of limonite and hæmatite. These bands are not true veins, but stains. The groundmass shows cracking similar to that seen in the plagioclase and quartz phenocrysts.

These rocks appear to be intermediate phases between the lithoidal hornblende andesites and the pyroxene andesites.

Lithoidal Varieties. There are two horizons of the hornblende andesite, a lower and an upper, the former being far thinner. Some phases of the upper flow contain more free quartz, otherwise both are fairly similar megascopically. In appearance the rock variation is the amount of deuteric action and weathering it has undergone. When fresh the rock is bright black in colour with fresh glassy phenocrysts of plagioclase, hornblende and biotite. The deuteric effects are revealed in the greyer groundmass and the whiter and duller phenocrysts of plagioclase and duller phenocrysts of hornblende. The very deuterically altered rock is a fawn colour with dull phenocrysts and in some cases it is a reddish brown colour with smaller phenocrysts. The hornblende andesite also varies megascopically in the proportion of salic and femic minerals. Some abound in both, others in comparison are lacking in one or the other, while still in others the phenocrysts of both are scanty.

Microscopically the hornblende andesite is porphyritic and contains phenocrysts of plagioclase, hornblende, biotite and more often than not quartz. Magnetite and apatite are accessory minerals.

The plagioclase is in the form of idiomorphic to subidiomorphic tabular crystals. Where it is unaltered it appears to be andesine ($\text{Ab}_{65}\text{An}_{35}$). Some crystals show strong composition zoning and in some cases zoning by decomposition and inclusions. Associated with albite twinning is often the pericline or Carlsbad type. The crystals which have been most albitized have also been partly chloritized towards the centre. In some instances the plagioclase has been completely pseudomorphed by chlorite. The albite has attacked the most basic part of the crystal or along the cleavage planes first. In some specimens the plagioclase is partly altered to kaolin. Most inclusions are of magnetite and apatite.

The hornblende is usually in idiomorphic prismatic form. It is of the green variety and is usually partly or wholly altered to chlorite and/or magnetite or limonite. One example from the lower flow shows the hornblende to be pseudomorphed by calcite surrounded by limonite and in some sections pseudomorphed by limonite.

Quite often biotite is present, and it too is often chloritized and/or replaced by an iron mineral.

Magnetite is abundant throughout and appears as phenocrysts or as inclusions in the phenocrysts of plagioclase, hornblende and biotite. It is also to be found scattered throughout the groundmass. It is possible according to Harker (1935) that much of the finely divided magnetite in the groundmass was derived from the breaking up of the hornblende and biotite during resorption of the groundmass.

Modal quartz is found in a considerable quantity in some rocks and where this occurs the hornblende andesites are more dacitic in character. The quartz usually is subidiomorphic in habit and shows resorption effects. It quite often contains pseudo inclusions of the groundmass and shows evidence of fracture.

Apatite is found as small idiomorphic crystals both as inclusions in the phenocrysts and in the groundmass.

The groundmass is generally cryptocrystalline and in some cases has a tendency to flow structure. In some cases the groundmass has small chloritized patches. Tiny vesicles filled with chlorite and/or chalcedony are frequently found in the groundmass.

Fragments of earlier flows and sedimentary rocks are commonly found in the hornblende andesite and in some instances the fragments represent cognate xenoliths which are actually portion of the first cooled part of the flow.

TOSCANITES.

Toscanites occur in both the Volcanic and Glacial Stages in the district. The two types vary both megascopically and microscopically. In some places the toscanites are more dacitic than toscanitic, depending on the amount of orthoclase present.

The toscanite of the Volcanic Stage corresponds with the Mt. Gilmore type and that of the Glacial Stage with the Paterson type in the Clarencetown-Paterson District (Osborne, 1925).

The toscanite of the Volcanic Stage is found on two horizons, the upper toscanite being a brownish colour and containing abundant phenocrysts of quartz and plagioclase with some orthoclase and a little biotite. It contains fragmental remains. The more weathered specimens are streaked with veins of limonite. The Paterson type is a bluish grey colour becoming brownish on weathering. It contains abundant phenocrysts of quartz, plagioclase and some orthoclase and biotite in a stony groundmass.

Microscopically the toscanites consist of phenocrysts of plagioclase, orthoclase, quartz and biotite in a light brown coloured groundmass.

The plagioclase is the most abundant felspar and is andesine $Ab_{63}An_{37}$. It occurs in subidiomorphic crystals, is partly albitized and kaolinized, and in places is also altered to sericitic material and chlorite. It shows zoning by decomposition.

Orthoclase is present in a smaller proportion than the plagioclase. It has simple twinning and has also been slightly deuterically altered to albite.

Quartz is fairly abundant and occurs in large subidiomorphic crystals which show resorption effects and contain pseudo inclusions of the groundmass.

The ferro-magnesian mineral is biotite, which is present in a small quantity. It is in the form of idiomorphic prismatic crystals. It is very dark in colour and is speckled with magnetite, which has probably been derived from the mineral. It also shows alteration to chlorite in some cases.

Magnetite is not very abundant and occurs as phenocrysts which show signs of resorption. It is altered to limonite in some cases.

Apatite is an accessory mineral and is found as inclusions and in the groundmass.

The groundmass is hypohyaline, being partly cryptocrystalline and partly glassy. It usually shows excellent flow structure and in some cases shows spherulitic structure. The latter feature is well seen in an example of the Paterson toscanite. The spherules are stained with limonite and as a result it is difficult to determine their composition. A tiny crystal of felspar or a tiny fragment of cryptocrystalline groundmass is often found as a nucleus for the crystallization of the spherules. The groundmass on the whole is stained in patches with limonite and contains patches of chloritic material.

DACITES.

Dacites are intermediate in composition between hornblende andesites and toscanites. Although some of the two latter types are dacitic in parts according

to the percentage of quartz and orthoclase present the only true dacite is a biotite dacitic pitchstone which occurs at the base of the top flow in the Volcanic Stage.

Megascopically the rock is black in colour and has a bright pitchy lustre. It contains phenocrysts of biotite and inclusions of other rocks. It is extremely brittle.

Microscopically the rock consists of phenocrysts of plagioclase, quartz and biotite set in a glassy groundmass.

The plagioclase is andesine ($Ab_{65}An_{35}$). The phenocrysts are subidiomorphic and tabular in form and show evidence of resorption. They also show strong albite twinning and composition zoning.

The quartz phenocrysts are subordinate in amount to the plagioclase phenocrysts. They show resorption effects and contain inclusions of the groundmass. It is in the form of subidiomorphic crystals.

Other phenocrysts are of brown biotite which show evidence of strain in the bending of some of the crystals. Evidence of strain is also revealed by cracking by the salic phenocrysts and the groundmass.

Inclusions of idiomorphic needles of apatite are present, also cubes of hæmatite.

The rock contains numerous inclusions which include for the most part pyroxene andesites and fragments of glass. Some of the inclusions show resorption effects and reaction with the groundmass and in some cases are surrounded by a halo of limonite. The inclusions vary in size from a fraction of a millimetre to 2 mm.

RHYOLITES.

The only true rhyolites in the district seem to occur at the base of the series, i.e. the two lowest acid flows. Megascopic descriptions of these types have been given in the description of the stratigraphy.

Microscopically the lowest rhyolite consists of phenocrysts of quartz which show resorption effects in a very light coloured groundmass. The groundmass shows a fine vermicular or imperfect spherulitic effect. Abundant small rounded vesicles filled with granulated chalcedony and calcite occur throughout the rock. Patches of carbonaceous material, probably weathered calcite, are present. The rock resembles a glassy type of rhyolite with vesicles which is becoming devitrified and amygdaloidal.

The John's Hill type appears to consist of phenocrysts of orthoclase and plagioclase which are now almost wholly decomposed to kaolin, albitized, chloritized and in some cases show saussuritization, in a groundmass which is glassy for the most part. Other parts are cryptocrystalline. It shows excellent fluidal fabric and in patches are concentrations of limonite. Where the felspar is cracked, hæmatite infills the cracks. Magnetite occurs as small phenocrysts. Veins of chalcedony are common throughout the rock.

KERATOPHYRES.

The keratophyres which are present in the Stanhope District appear to be andesites which have been completely albitized by late magmatic solutions.

A typical keratophyre occurs above both flows of hornblende andesite. In the hand specimen it is a purplish grey colour with rectangular shaped phenocrysts of plagioclase. Microscopically it is seen to consist of tabular idiomorphic phenocrysts of albite in a cryptocrystalline groundmass. The plagioclase is much altered to kaolin and shows zoning by composition and decomposition. Magnetite is fairly abundant as fine grains and as larger crystals.

TRACHYTES.

The only trachytes in the district occur at the top of the Upper Glacial Stage and outcrop at Cranky Corner and to the north-east of it. They appear to occur in three flows; the lowest is porphyritic and is purplish grey in colour and contains larger phenocrysts of plagioclase. It is more in the nature of a trachyandesite.

Microscopically the porphyritic stage consists of phenocrysts of plagioclase and a few of augite in a groundmass of tiny tabular crystals of felspar which give rise to a trachytic fabric. The phenocrysts of plagioclase are tabular idiomorphic crystals which have been completely albitized. The augite is in subidiomorphic prismatic crystals and in places has been silicified. Magnetite is fairly abundant. The groundmass consists of tiny idiomorphic crystals of felspar which for the most part is orthoclase and some plagioclase. Both have been somewhat albitized. The orthoclase crystals show simple twinning. The crystals in the groundmass give rise to a trachytic fabric. Tiny vesicles in the rock are filled with chlorite and chalcedony.

The middle flow consists of a greenish grey fine-grained trachyte. A section of this fine-grained trachyte shows good trachytic fabric and consists of tiny tabular shaped crystals which have been partly albitized and chloritized. The felspar crystals vary in size and show simple twinning. Chlorite is interstitial. Abundant cubic crystals and grains of magnetite are present. Apatite is present in a very minute quantity. Carbonaceous material is scattered about in the groundmass. The rock has been much deuterically altered.

The top flow of the trachytic series is amygdaloidal, the amygdules consisting of chalcedony, calcite, chlorite and zeolite. The fresh rock is a greenish grey in colour and weathers to a dark reddish brown type and on further decomposition to a khaki coloured rock in which the amygdules are stained or replaced by limonite. The rock in parts is quite vesicular.

Microscopically the rock consists of phenocrysts of plagioclase, hornblende and some augite in a groundmass composed of tiny crystals of plagioclase, orthoclase, augite and iron ore. The plagioclase is in idiomorphic lath-shaped crystals and is of two sizes, the larger as phenocrysts and the smaller taking their place in the groundmass. The plagioclase has been completely albitized and in a few instances is partly chloritized towards the centre. It is impossible to determine the original type of plagioclase.

Hornblende is the next abundant phenocryst, and is very subordinate to the felspar. Some pieces are partly chloritized. It is in subidiomorphic form.

Pyroxene, hypersthene, gives rise to a few small phenocrysts and is in subidiomorphic form. This mineral forms tiny grains in the groundmass.

Other constituents in the groundmass are iron ore, which is quite abundant, and probably orthoclase. It is very difficult to definitely recognize orthoclase from plagioclase in the tiny crystals on account of the great amount of albitization. The rock contains numerous vesicles which have been infilled by secondary material, giving rise to an amygdaloidal rock. These secondary materials have been named in the megascopic description of the rock.

DACITE AND RHYOLITE TUFFS.

These tuffs are to be found on several horizons. Megascopically they resemble rhyolites.

Thin bands of dacite tuffs occur in the Volcanic Stage. The best and thickest development of them is associated with the dacitic pitchstone at the top of the Volcanic Stage.

Megascopically the tuffs are pink in colour and contain phenocrysts of biotite and fragments of foreign material.

Microscopically the rocks consist of phenocrysts of plagioclase, quartz and biotite in a groundmass of cusped fragments of devitrified glass. These fragments are stained with limonite and are welded together. Inclusions of basalt, shale and unstained glass appear in the groundmass.

The rhyolite tuffs can be divided into two groups, the first being characterized by a greater proportion of plagioclase than orthoclase and the second by those in which the amount of orthoclase is greater than plagioclase. The two upper bands of rhyolite tuff in the Glacial Stage are typical of the latter group, while the top rhyolite tuffs of the Volcanic Stage and the lowest rhyolite tuffs in the Glacial Stage are characteristic of the first.

Sodipotassic Rhyolite Tuffs.

The megascopic characteristics of these rocks have been briefly described in the stratigraphy. Microscopically these tuffs are composed of phenocrysts of quartz, plagioclase and some orthoclase and sometimes a little biotite in a groundmass which is usually glassy and shows signs of devitrification.

The quartz usually shows resorption effects and contains pseudo inclusions. The felspar is generally albitized to a certain degree and kaolinized. Plagioclase is in a greater proportion than orthoclase and is acid oligoclase. The groundmass is generally kaolinized and is stained with limonite. It shows good flow structure.

Potassic Rhyolite Tuffs.

As stated above, the rhyolite tuffs which come under this heading are those forming the two upper flows in the Glacial Stage. The megascopic characters of the rocks have been briefly given in the stratigraphy.

Microscopically the potassic rhyolite tuffs contain abundant phenocrysts of quartz and felspar, the greater part of which is orthoclase, and some biotite in a groundmass which shows signs of devitrification.

The quartz is usually in subidiomorphic prismatic form, shows resorption effects, and often contains pseudo inclusions of the groundmass. Sometimes the quartz is in angular fragments which also show resorption effects.

The felspar most predominant is orthoclase, which is usually altered to a greater or less extent to kaolin and is often stained with limonite. Some crystals show simple twinning. Plagioclase is less abundant and when present is usually in small crystals and shows albite twinning. Both felspars are somewhat albitized.

The groundmass of these rhyolite tuffs is usually kaolinized and stained with limonite. On the whole it usually shows excellent flow structure and consists of cusped fragments of glass and felspar. The structure of the groundmass seems to indicate a collapsed pumice. See Figure 3 A and C.

Ignimbrites.

Although these rocks are a type of rhyolite tuff, microscopically they have a slightly different aspect from the characteristic type of rhyolite tuff prevalent in the district. They occur at the top of the Volcanic Stage and some of the lower felsites in this stage are actually ignimbrites. Megascopic descriptions have been given in the description of the stratigraphy.

Microscopically this type consists of phenocrysts of quartz, plagioclase which is oligoclase ($Ab_{20}An_{30}$) and orthoclase, with a little biotite in a groundmass. The groundmass is composed of abundant shreds of glass and felspar welded together, and shows flow structure. See Fig. 3B. It sometimes shows comb and spherulitic structures. Furthermore, it is usually kaolinized and in parts stained with limonite. Often fragments of other volcanic rocks and glass are present.

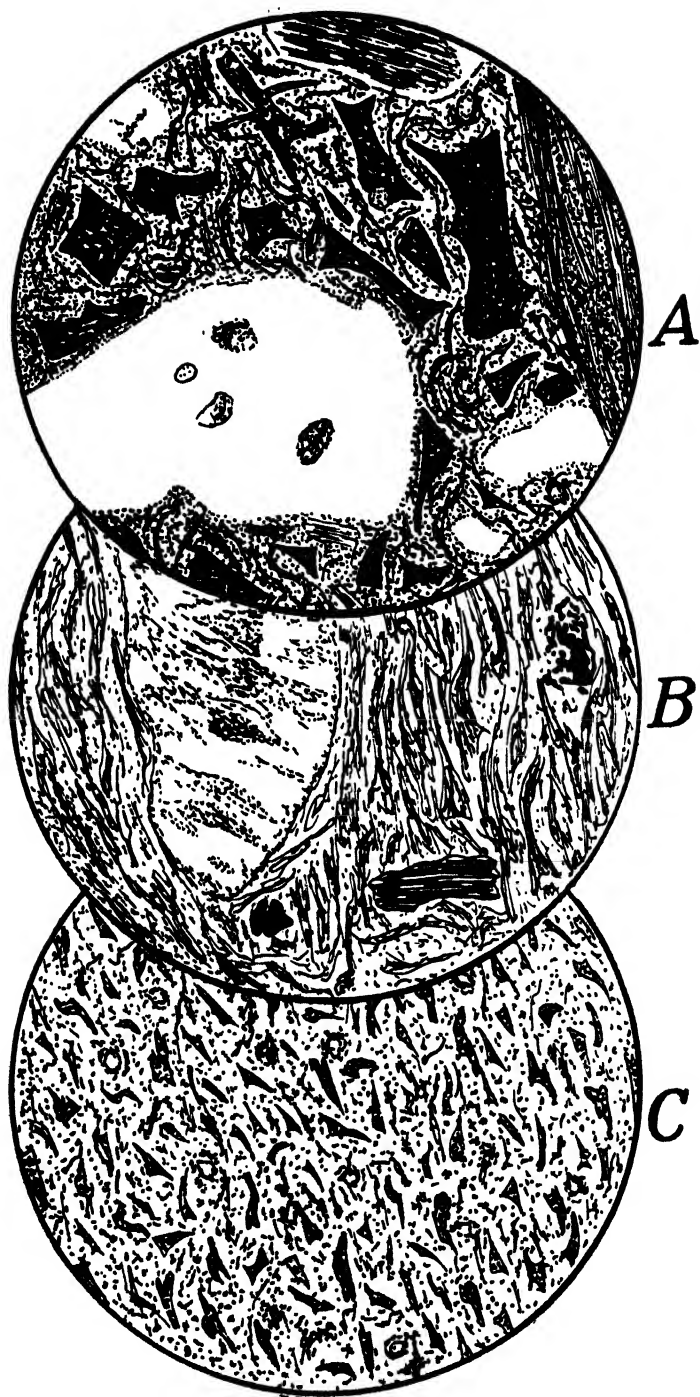


Fig. 3.

A. Rhyolite Tuff. $\times 30$.

B. Ignimbrite. $\times 25$.

C. Rhyolite Tuff. $\times 70$.

TUFFS (OTHER THAN RHYOLITE TUFFS).

The tuffs of the Volcanic Stage are for the most part pink in colour and are very felspathic. They vary in grain size from extremely fine to moderately coarse. The fragments consist of quartz, plagioclase, orthoclase, biotite and tiny dark fragments of rock. Some fragments are much larger than others and are up to half an inch in width. Other tuffs have a purplish colour and contain abundant fragments of white plagioclase, pink orthoclase, quartz, biotite and other rock fragments. These seem to occur more above the hornblende andesites, whereas the pink ones are above the felsites.

The tuffs of the Glacial Stage are also very felspathic and in places are extremely siliceous and micaceous. They vary in colour from pink to light brown, and may be either very tough or quite friable. A green siliceous felspathic tuff is fairly common but does not give rise to very thick bands. Microscopically a typical example of a pink tuff contains abundant small angular fragments of quartz and felspar which is decomposed for the most part and an abundance of limonite. The matrix is kaolinized. The pink colour of the tuffs is due to the presence of hæmatite and limonite.

At the top of the Upper Glacial Stage associated with the trachyte flows is a trachyte breccia which consists of angular fragments of trachyte of varying sizes. This is the only true breccia which was found in the district.

THE EFFECTS OF LATE MAGMATIC SOLUTIONS.

Three types of magmatic or deuteric alteration, namely albitization, chloritization and deutericization, are prominent in the Kuttung lavas in the district.

Albitization.

The albitization of the feldspars in the Carboniferous lavas in the Stanhope District could well be used to illustrate the paper by Bailey and Graham (1909) in which they ably expressed their views on the albitization of plagioclase feldspar. Browne and White (1926) describe the albitization of the Blair Duguid hypersthene andesite, a Kuttung lava, and record albitization as having been produced by cognate solutions during the last stages of crystallization.

It was found that the hornblende andesites, toscanites and rhyolite tuffs were the most albitized and the pyroxene andesites were only partially albitized. On the other hand the pitchstone phases of the andesites are relatively free from deuteric action. This is probably due to the fact that the solutions were unable to percolate through the glassy groundmass. It is found that the albite generally attacks the edges of the crystals and works its way along the cleavages. In some cases the feldspar has been completely albitized, while in others it has been only partially replaced. It is a noticeable fact that the albite attacks the most basic feldspar first. For instance the phenocrysts which are the first to form and so more basic than the minute crystals of the groundmass, are attacked first. Also in zoned crystals the most basic zones, noticeably those towards the centre, are attacked first. This fact helps to point out that the soda effecting the albitization belonged to the magma itself, as the pyroxene andesites which are the most basic rocks in the area are least deuterically altered. If the effect was due to meteoric solutions then the plagioclase of the pyroxene andesites would have suffered to a greater extent.

In some cases associated with the albite are tiny flakes of sericitic material which is probably a weathering product of the albite. The albite appears to have a rough surface due to the aggregation of the tiny particles of albite and possibly other material which is replacing the plagioclase. Mostly the change takes place molecule by molecule, and as a result the optical properties of the

original plagioclase remain. If the replacement is not complete it may be possible to determine the nature of the original residual plagioclase.

More often than not in the rhyolite tuffs the orthoclase felspar has been replaced in a patchy fashion by the albite and has a dirty yellowish brown appearance due to iron staining. This staining of the albite is particularly noticeable in the cusped fragments of orthoclase in the pumiceous groundmass.

Chloritization is very often associated with the albitization and this phenomenon helps to indicate that the solutions which effected the albitization were cognate and not meteoric.

Chloritization.

In the Kuttung lavas in the district chloritization as well as being associated with the albitization of the plagioclase is also associated with the ferro-magnesian minerals. Hornblende is especially susceptible to chloritization, also biotite, whereas pyroxene is generally only altered about the edges. In some cases where chlorite has pseudomorphed the hornblende, calcite is in association. This is probably due to the lime separated from the hornblende during the replacement by chlorite. In a section of a rock from the middle pyroxene andesite flow where the ferro-magnesian, probably a pyroxene from the crystal outline, has been pseudomorphed by chlorite, calcite is quite abundant. It is unusual to see the pyroxene so altered to chlorite.

Although chlorite may also be associated with ordinary weathering, an examination of the rest of the rock will usually indicate its origin, as deuteric effects are also usually suffered by the plagioclase. The chlorite replaces the plagioclase towards the centre and sometimes along cleavage planes. Where chloritization is closely associated with albitization its origin may safely be regarded as due to late magmatic solutions.

Patches of chlorite in the groundmasses of the andesites seem to indicate a replacement of some indeterminate material.

Kaolinization.

In spite of the fact that kaolinization is mostly a weathering product, in the Kuttung lavas it must also be regarded as a phenomenon resulting from late magmatic solutions. The groundmasses of most of the rhyolite tuffs have been kaolinized and also the felspar phenocrysts to a certain extent. Certainly some of the kaolinization is due to ordinary weathering, but not all, the other being due to late magmatic origin. Often the kaolin is stained with limonite and is a yellowish brown colour.

DEVITRIFICATION.

Devitrification has occurred in a great number of the volcanic rocks in the district.

Evidence of devitrification is in a number of forms such as spherulitic and axiolitic structures and alteration of the glass into cryptocrystalline material in a patchy fashion. The rhyolite tuffs show excellent examples of devitrification. The groundmass contains pumiceous material which was originally glassy but has now been wholly or partly altered to cryptocrystalline material. In some of the rhyolites and toscanites the groundmass contains patches of cryptocrystalline material in the glass which can definitely be distinguished from the streaks of glass in some of the other volcanic rocks. The latter case is not due to devitrification but to the fact that the glass did not crystallize out with the rest of the rock due to the heterogeneity of the magma after the phenocrysts had crystallized.

Spherulitic and axiolitic structures are present in some of the toscanites, rhyolites and rhyolite tuffs. The spherules can only be seen microscopically

and show up best in crossed nicols. They appear to be radiating fibres of felspar with possibly some quartz which often show a tiny felspar crystal or a tiny portion of crystalline groundmass as a nucleus. Axioilites do not consist of radiating fibres but of fibres more or less arranged in a parallel fashion. Whereas crystallization commences from a point in spherulitic structure, it commences along a line in axioilitic structure.

Bonney and Parkinson (1903) described two types of devitrification, one primary and one secondary. They mention that axioilitic structure and some spherulitic structures are indicative of primary devitrification and the patchy type of secondary devitrification. From the evidence available in the Stanhope District it appears as though both are present, sometimes alone and sometimes secondary superimposed upon primary. Bonney and Parkinson, however, fail to give the times of the two types of devitrification but according to Osborne (1925) Bonney, in another paper, indicated that the primary devitrification occurs during cooling and the secondary type long afterwards. In the lavas examined there is little evidence to indicate when devitrification occurred. It is possible that some of it at least may be connected with the activity of late magmatic solutions.

The cause of devitrification is another moot question. Anderson and Radley (1915) agree that there are two types of devitrification and have postulated the following theories for their formation. In primary devitrification where the limits are sharp the process is due to the escape of water very soon after solidification while the rock was still warm. Secondary solidification according to them is due to the later and very gradual penetration of water or possibly other reagents which they do not state. Bonney and Parkinson consider that for primary devitrification the following physical conditions are required—a low pressure with active water content, an initially high temperature and rapid fall. Parkinson suggests that secondary devitrification begins by hydration of the glass in the neighbourhood of perlitic cracks.

In dealing with devitrification a question arises as to whether the lithoidal andesites are the devitrified equivalents of the glassy andesites. As no chemical analyses have been carried out it is impossible to determine the chemical relationship between the two varieties. However, field evidence suggests this is not the case and that both varieties form distinct flows. In the field one would expect to find gradations from glassy to lithoidal types but this is not the case as the glassy phase passes abruptly into the lithoidal phase in all the flows concerned. Also microscopically, if the lithoidal is the devitrified glass, then one would expect to find microscopic evidence in the form of residual glass in the groundmass. On the contrary, no residual glass has been found in the groundmasses of the lithoidal types. It seems, therefore, that the lithoidal types are quite independent of the glassy types.

VOLCANIC HISTORY.

The Carboniferous period, particularly during Kuttung times, was one of the greatest periods of volcanic activity, and great thicknesses of volcanic lavas and tuff were ejected. Two types of volcanic action are evident in the district. In the first place, there are the lava flows which have poured quietly over the surface represented by the andesites, toscanites and rhyolites, and secondly the explosive type represented by the ignimbrites, rhyolite tuffs and other tuffs.

No evidence of a centre of eruption is present in the district, but from the nature of the outcrops of the lava flows the centre of eruption appears as though it was towards the north-east of the district.

During the earlier stages of the volcanic history the eruptions must have been alternately of the quiet and explosive types, the former represented by the lava flows and the latter by the accumulations of volcanic tuff found in between

the flows. Volcanic action in the latter part of Kuttung times was mostly of the fragmental type, as represented by the rhyolite tuffs, as the only important flow is that of the Paterson toscanite.

Accompanying the volcanic activity was glacial action which enabled much of the volcanic ash to be carried along by the glacial streams. Lava flows and tuff were poured out over the glacial and aqueoglacial accumulations, as it is quite common to see beds of tuff or of lava flows immediately overlying the fluvio-glacial conglomerate, tillites and varves.

The true lava flows are more basic in character than those rocks resulting from the explosive type of eruption. They have flowed over the land surface gathering as they went fragments of underlying material. If the flow was of an intermittent nature the surface sometimes cooled quickly and pressure from the lava, when it began to flow again, often caused the crust of the flow to be broken up and caught up in the lava. Evidence of this is seen in the hornblende andesites. It is only natural to expect that these cognate xenoliths and fragments must have caused a certain amount of contamination when they were assimilated or partly assimilated by the lava. Evidence of steam or gas holes, formed when the gaseous substance escaped, is present in the form of vesicles which in most cases have become filled with secondary material.

The ignimbrites according to Marshall (1935) are deposited from immense clouds or showers of intensely heated but minute fragments of volcanic magma. The temperature of these fragments is thought to have been so high that they were viscous and on reaching the ground adhered together and formed a "lava" which was capable of flowing.

The rhyolite tuffs found in the Upper Glacial Stage indicate explosive types of eruptions as they contain numerous cusped fragments of glass which are sometimes devitrified and welded together. These rhyolite tuffs are characteristic of collapsed or broken pumice. The embedded crystals of quartz and feldspar present in most types were formed earlier in the magma reservoir before eruption. These tuffs have evolved from a very acid magma which, after having been shattered in the air, was capable of flowing after having been welded together on reaching the surface. The rhyolite tuffs differ from ignimbrites, the latter having uniform and normally fine texture, while the former are coarser and more fragmental.

The trachyte flows, the last lava flows in the Kuttung, probably originated from a different vent which may have been situated in the vicinity of the trigonometrical station just east of Cranky Corner as here is to be found an abundance of coarse trachyte breccia, and it is here that the flow seems to attain its maximum thickness.

MINERALOGICAL AND GENETIC RELATIONSHIP.

Generally speaking the whole series of volcanic rocks of the Kuttung in the district is fairly acid, the types not containing free quartz are the pyroxene andesite, which is the most basic, and the alkaline trachytic type at the top.

The types of plagioclase feldspar gradually increase in acidity from labradorite $Ab_{48}An_{52}$ in the pyroxene andesites to oligoclase $Ab_{73}An_{27}$ in the sodipotassic rhyolite tuffs. As considerable albitization has taken place, it is not possible to say whether any primary albite occurs in the rocks. The albitization also makes determination of the plagioclase difficult.

The potash feldspar, orthoclase, is absent from the andesites but makes its appearance in the toscanites and the sodipotassic rhyolite tuffs above the toscanite. In the latter orthoclase is greater in amount than plagioclase. The trachyte consists almost wholly of orthoclase.

The ratio of ferro-magnesian minerals to salic minerals in all types is small. It decreases from basic to acid types. Biotite is the most widespread of the ferro-magnesian minerals.

Augite and hypersthene, apart from occurring in the pyroxene andesites, are not found in other types with the exception of the hornblende andesitic pitchstones where they occur with the hornblende. A little has also been found in the andesitic phase of the trachyte.

Iron ore, which consists of magnetite and ilmenite, is fairly abundant throughout, as is apatite.

The mineralogical relationships seem to indicate that the lava flows with possibly the exception of the trachyte are magmatically related.

As no plutonic rocks related to the volcanic rocks have been found in the district nothing can be said of the type of primary differentiation. Iddings (1896) records Brögger as saying that even after portions of the magma have been separated from the parent magma by being erupted into deep-seated parts of the earth's crust, further differentiation may take place in these portions producing basic and acid rocks which may be extruded upon the surface of the earth. A series of eruptions from one of these portions would therefore not be the same as a series from the original magma basin. This indicates that the order of eruption of extrusive rocks is for the most part dependant on relatively secondary differentiation. From field and mineralogical observations of the volcanic rocks in the district it appears as though the parent magma was in the nature of a hornblende andesite from which differentiated more basic and more acid types.

It is possible that the trachyte flows could have originated from the same magma chamber as the calcic types, being the alkaline fraction which was extruded through the same or a different vent from the calcic lavas.

STRUCTURAL GEOLOGY.

Folding.

The basin structure in the area under discussion is shown by the dips indicated along the various flows and beds and the direction of outcrops of the beds. It is also well indicated by the physiography described above.

The beds of the Volcanic Stage do not turn to the north towards the east but continue in a south-easterly-north-westerly direction and form part of the Lochinvar anticline. The amount of dip of the beds on the whole is fairly constant, varying for the most part between 30°-40°. The Permian rocks which have given rise to the Cranky Corner basin have been deposited conformably upon the Kuttung rocks.

The basin in the Stanhope District, known as the Cranky Corner Basin, is separated to the east from the Moonabung Basin, described by Osborne (1927), by a plunging anticline out of which Lamb's Creek has carved its valley. This anticline is really the northern part of the Lochinvar anticline and pitches to the north. The northern portion of the basin has been faulted against the Mirannie Basin, described by Osborne (1926), by the Webber's Creek fault. Osborne (1926) considers that the Cranky Corner Basin may be a faulted portion of the Mirannie Basin, that is both being portions of a large basin which existed before the Webber's Creek fault. He accounts for the relative positions of the two basins at the present time by lateral movement either in an easterly direction on the Cranky Corner side or in a westerly direction on the Mirannie side during faulting. In the south and south-west corner the basin is cut by the Hunter overthrust fault as well as by smaller minor faults.

There is no evidence in the area examined as to the exact age of the diastrophism apart from the fact that it is post-Permian, probably at the end of Palæozoic time, as the Permian beds are conformable upon those of the Car-

boniferous and appear to have been folded with them. According to Osborne (1929) in the Paterson-Wallarobba and Scone Districts there are outliers of Tertiary basalt overlying the remnants of a peneplain which was carved out of the folded and faulted Kuttung and Burindi rocks indicating that the folding and faulting are older than the basalt. From his study of the relationship between the Triassic and Permian formations to the south, David (1907) states that the folding began in Upper Marine times and was completed before the deposition of Triassic sediments.

Faulting.

Faulting is an important structural feature in the Hunter River District. The folded structures which antedated the faulting have been cut by numerous faults. In the Stanhope District the largest and most important faults are the Hunter overthrust and the Webber's Creek fault. In this area the Hunter overthrust fault was originally considered to consist of two parts, the Lachnagar and Elderslie faults. It trends in a general north-west-south-east direction along the Hunter River and then cuts across the Kuttung lavas until it meets Dutton's Creek. It is here dislocated by a smaller fault and is found again near the Hunter River, whence it trends in an east-west direction to Elderslie, where it is again dislocated before turning to the north. From here it trends in a northerly direction until a little before reaching Brook's Mountains, when it trends north-west, continuing in this direction until it meets the Bridgeman-Webber's Creek fault. The Webber's Creek fault has been described by Osborne (1926).

Towards Elderslie are a few minor faults, probably tear faults in the weakened portion of the earth in the vicinity of the major fault.

In the Stanhope District there is no evidence to indicate the nature of the fault, but evidence available elsewhere indicates that the Hunter overthrust fault has a throw of approximately 5,000 feet. This fault has caused Permian strata to be thrust against the Kuttung rocks.

Throughout the whole area slickensides are predominant, indicating earth movements. These are especially noticeable along the Cranky Corner Road, but there is no other evidence such as a break in the continuity of the beds to indicate a major displacement such as a fault.

The faulting is younger than the folding. Its age can be set between two limits, the upper limit being set at pre-Kosciusko Uplift as faulting did not take place during this uplift. If it had, the faulting being of such a magnitude, would have revealed itself by fault scarps, none of which are present in the district. The only relationship between the physiography and the faults is that the streams have sought out the planes of weakness along which to carve their valleys, and resistant Kuttung lavas have been brought up against softer Permian rocks. The lower limit of their age is just after the age of the folding.

SUMMARY.

The rocks of the Stanhope District are of Kuttung and Permian age and have been folded into a basin structure at the close of the Palæozoic era.

A great thickness of volcanic and glacial beds constitutes the Kuttung. It has been decided that, unlike the type area, the Kuttung rocks cannot be satisfactorily divided into the Basal, Volcanic and Glacial Stages, as both glacial and volcanic conditions were persistent throughout.

The Permian rocks near Cranky Corner rest conformably upon the Kuttung rocks, while those to the south and the west of the area have been brought up against the Carboniferous strata by the Hunter overthrust fault.

Brief petrographical descriptions of the rock types have been given, and from a study of these it is found that the rocks vary from acid to basic volcanic

and are related magmatically. They have been ejected by two different types of volcanic activity. From field and mineralogical observation it appears that the parent magma was in the nature of a hornblende andesite which differentiated into acid and basic phases.

ACKNOWLEDGEMENTS.

In conclusion, the writer wishes to express her appreciation of the hospitality and kindness tendered to her during her trips to the area. She would particularly like to mention the kindness of Mr. and Mrs. M. H. Standen of Stanhope, and Mr. and Mrs. P. Grainger and family of Glendonbrook. She is also indebted to Dr. G. A. Joplin for her kind criticism and helpful suggestions in the preparation of the manuscript.

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THE GENERAL GEOLOGY OF THE BOMBALA DISTRICT, N.S.W.

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With Plate VI and three text-figures.

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I. INTRODUCTION.

The town of Bombala, situated on the Monaro Tableland, 330 miles by rail south from Sydney, is the centre of one of the prosperous sheep and cattle raising districts for which the Monaro is famous.

There is no record of any previous geological work in the area, except that it is represented on the state geological map as consisting of Devonian sediments and of granite, with a capping of basalt to the north and south of the town.

Extensive geological studies were carried out around Cooma, over 50 miles north of Bombala, by Browne (1914 and 1943) and by Joplin (1942 and 1943), while nearly 40 miles to the east investigations on the Devonian rocks have been made by Brown (1931). At Quidong, 16 miles south-west of Bombala, Silurian

sediments carrying a considerable fossil fauna have been recorded (Carne and Jones, 1919) but no detailed mapping or collecting has been done in this area. Sussmilch (1914) also makes brief reference to the extensive development of basalt between Cooma and Bombala.

An account of the general geology of the area will be given here.

II. GENERAL GEOLOGY.

The area examined includes a tract of country of some 70 square miles in which an interesting variety of rocks has been found. These comprise unfossiliferous sediments of Ordovician and Devonian age, the former having suffered a low grade of regional metamorphism and in places a superimposed contact metamorphism. No Silurian sediments occur within this specific area, but to the south-west they occur unconformably above the Ordovician rocks and carry a prolific fauna. Tertiary river gravels are common and are frequently overlain by basalt, which covers large areas to the north of Bombala as well as isolated patches to the south. Most of the basalt in the south has now been eroded, only a few small peaks being left as residuals surrounded by more widespread grey billy.

Igneous rocks of both plutonic and hypabyssal types occur, the former as parts of a composite batholith and the latter as dykes. The hypabyssal rocks are grouped around two principal centres—one within the limits of the town itself and called for convenience the "Hospital Porphyries", and the other some three miles to the west, forming the prominent Paradise Hill and penetrating the surrounding rocks in dykes for distances up to three miles. Both these masses are in part garnetiferous.

There are three principal plutonic types forming distinct masses—a coarse acid granite (the Bukalong Intrusion), a granodiorite (the Coolumbooka Intrusion), and a quartz mica diorite (the Bombala Intrusion). Within the Bukalong complex are a number of rock types, some of which are undoubtedly contaminated. The Bombala and Bukalong intrusions have been mapped in detail but only the southern tip of the Coolumbooka mass has been included and its full extent is unknown. The detailed petrology of the igneous rocks will not be attempted here.

III. SEDIMENTARY AND VOLCANIC ROCKS.

The sedimentary rocks are of three ages—Ordovician, comprising steeply-dipping "slates", as they are locally called, an overlying series of gently-dipping Devonian conglomerates, grits, sandstones and shales, and a third group of Tertiary sediments of more limited extent.

(a) *Ordovician.*

Rock Types.

The nature of the sediments which make up the Ordovician strata is variable and includes all gradations between fine pelitic sediments (Joplin, 1942) and coarse sandy and gritty psammitic beds. A considerable number of these are apparently tuffaceous in character. In the western part of the area a few narrow bands of black slate have been found. One of these is a highly pelitic type, the other is more psammitic. These strongly resemble the graptolite-bearing slates of the Cooma district, which are considered by Joplin (1945) to be of volcanic origin. Graptolite-bearing black slates of similar age (Upper Ordovician) are also recorded some 25 miles south-west of Bombala at Tingaringi and Currowang (Hall, 1902). A band of siliceous slate about two feet thick occurs beside the Bibbenluke Road some two miles from the town. It is dark and chert-like in appearance and thin section suggests that it formerly carried

radiolaria, but these are now unrecognizable. Most of the rocks within the area mapped have suffered a certain degree of contact metamorphism with the production of hornfelsed and spotted types.

Structure.

The structure of the Ordovician strata is difficult to determine, as it is impossible to follow an individual bed for any distance. The rocks are gently folded over most of the area, and small-scale faulting is seen in places. This is frequently accompanied by the development of slate-breccias along the fault planes. Minor folds and faults of hand-specimen dimensions are also found. Jointing is strongly developed and the tendency of the rocks to cleave along directions other than the bedding plane increases the difficulty of structural mapping. Folding is commonly seen in the strata, especially in the river sections, the width across the folds being usually of the order of 200 to 300 yards. The surface outcrop of one such fold is seen on the southern side of the Coolumbooka River at the Reservoir. The whole structure may be simply a series of these minor folds, but their irregularity and variation of axial direction suggest that they are rather a cross-warping upon a major structure. At Cooma the general strike of the Ordovician rocks is a little west of north. Here the strike directions are somewhat variable, but the general trend of the main axis of folding also seems to be in a direction west of north. The rocks on the whole are not steeply inclined, the angle of dip averaging about 40° to 50° . No strike and dip readings have been recorded on the map (Plate V) since it is felt that isolated readings could not give a true picture of the structure.

Correlation.

The fact that these slates occur unconformably below the Silurian beds at Quidong, together with their similarity to Upper Ordovician sediments in other areas, and especially their proximity and similarity to those at Cooma, places them almost without doubt as Upper Ordovician in age. The very finely cleaved pelitic rocks are almost identical with some of the low-grade Cooma pelites, and sandy and banded types also resemble some of the Binjura beds at Cooma. On the whole, however, these sediments are not typical of the Binjura beds, for they evidently contain a large amount of tuffaceous material and are often much coarser than the normal Binjura types. In addition, the differences are too pronounced to be explained as facies variations. This puts them into either the Coolringdon or the Bransby Beds, unless they constitute yet another series. The Coolringdon Beds on the one hand are almost entirely sedimentary in character, while the Bransby Beds contain a large amount of igneous material, tuff and limestone. No limestones or volcanic rocks are found here, and the beds are therefore placed temporarily with the Coolringdon Series.

Metamorphism.

Regional Metamorphism. The whole series has suffered a low grade of regional metamorphism and there is also a contact aureole along each of the igneous contacts. Thin sections show rocks varying from typical fine grained chlorite-sericite schists of low grade type to more siliceous and tuffaceous types with a matrix of chlorite, sericite and quartz. Thin section of a tuffaceous type shows irregular quartz, feldspar and rock fragments which on the whole are surprisingly little recrystallized. Many of the quartz grains indeed are barely changed.

Regional metamorphism in this area has thus produced rocks which are at highest in the chlorite zone. It is of interest to note, however, that the section of a rock on the Quidong Road in the Parish of Ashton revealed the presence of

biotite. No granite is known in this vicinity, although it may occur below the surface, and it is thus possible that the biotite was not formed by contact metamorphism. In addition, rocks along the Snowy River Road west of the Bukalong granite suggest a possible increase in metamorphic grade. As the place of the biotite zone in the metamorphic history at Cooma remains uncertain, examination of Ordovician rocks in this region may prove fruitful.

Contact Metamorphism. No true hornfelses have been formed in this area and original quartz fragments are often only partly recrystallized even at the igneous contact where red-brown biotite is developed in the matrix. The original schistosity becomes more prominent away from the contact but is always fairly well preserved. Spotted types appear in the outer parts of the contact aureole and seem to be restricted to the more pelitic types. A green mica occurs in place of the red-brown biotite away from the contact and is a prominent constituent of the spots. Distinct crystal outlines suggest that the spots were originally cordierite(?) but they now consist of the same minerals as the rest of the rock. No individual band can be traced through the varying stages of alteration and it is thus impossible to determine the exact changes which take place. The outer limit of the biotite seems to be almost coincident with that of the spotting so that this has been largely used as the criterion for determining the contact zone in the field.

(b) *Devonian.*

Rock Types.

The south-eastern part of the area is made up of sediments of Devonian age. A narrow strip carries northwards as far as the Reservoir and a small outlier also occurs beside the Bibbenluke Road west of the High Lake. Another outlier occurs near the village of Bibbenluke, ten miles north of Bombala, but mapping has not been extended as far north as this.

The beds, which are over 1,000 feet thick within the area examined, are made up of a variety of sedimentary types. The most common are grits—purple, red, grey or cream—while coarse massive conglomerates, sandstones and quartzites are also abundant. In addition to these a very characteristic rock is a red mudstone which occurs in intermittent bands throughout the series. The red beds are prominent in the basal parts of the series, where they form bands varying from only a few feet to 20 or 30 feet in thickness. At the Porphyry Quarry near the Hospital, for example, the basal Devonian beds are of red shale with an aggregate thickness of about 30 feet. These are overlain by 20 feet of conglomerates which are separated again from the thicker conglomerate capping (about 40 feet) by a further five feet of red shale.

The massive basal conglomerates which are well exposed amongst the interbedded sandstones, grits and mudstones above the Ordovician sediments on the Buckey Springs Road and again near the Reservoir turnoff on the Cathcart Road, appear to be rather more siliceous on the whole than those higher in the series and forming the hills further east. The sandstones and grits of the latter beds, however, are frequently very siliceous and may be more of the nature of quartzites. Whether or not this is related to any of the igneous activity which followed the Devonian era is difficult to decide. Similar quartzites have been described by Brown (1931) in corresponding beds on the coast further east, so that it seems to be some inherent feature of the sediments themselves. The distribution of the siliceous in contrast to the more normal sandstones appears to be purely fortuitous.

White mica is often developed along the bedding planes of the sandstones and the cementing material in most of the rocks is at least partly ferruginous.

Broadly speaking the series is divisible into three parts.

The lower stage has a thickness of about 150 feet and consists principally of massive siliceous and gritty conglomerates with interbedded red sandstones and mudstones. Purplish or reddish colours are common in the grits, while occasional buff-coloured types are also found. These beds of the lower stage form a rather prominent bluff facing the town, but fall away in a dip slope to the east. They swing eastwards near the Buckey Springs Road and front the Coolumbooka granite along its southern margin.

They are followed upward by a very much less resistant band which forms the cleared country along the Buckey Springs Road. Outcrops are often difficult to find except where a hard band forms a distinctive outcrop, but here the series appears to consist principally of red shales with a few conglomerates and some coarser sandstones, also of reddish colour. Behind the scarp formed by the basal beds, and the more prominent scarp of the upper conglomerates, this cleared area continues southwards, although of narrower width. Here, however, it is quite devoid of outcrop, but it is assumed that this too is part of the red shale horizon. The thickness of this stage is rather difficult to estimate, but it seems to be of the order of 200 feet.

The topmost stage here is the most prominent, forming a second and much higher scarp. South-east of the town this rises at first by relatively gradual increments, mainly over purple grits which are probably of tuffaceous character. With the appearance of bands of more resistant siliceous grits and sandstones, small vertical bluffs are formed, at first only about five feet high, but increasing in thickness towards the top so that they are often 20 feet or so high. They are separated by narrow bands of less resistance. The maximum thickness of these upper beds is 900 feet.

The total thickness of the series here is thus at least 1,200 feet. The conglomerates contain principally pebbles of quartz, quartzites and black slaty rocks evidently of Ordovician origin, in a gritty matrix. In many of the conglomerates, however, pebbles of Devonian rocks also occur, these being of gritty, sandy or shaly type and characterized by the red or purplish colour typical of the Devonian sediments. These are due either to brecciation under water of sandy or shaly bands forming contemporaneously, or else they are derived from earlier Devonian rocks exposed and consolidated.

Structure.

Two main difficulties have been encountered in the structural mapping of the Devonian strata; firstly the dying out of many of the beds, making it impossible to map one particular band for any distance; and secondly the frequent occurrence of current bedding, which may easily be mistaken for true bedding at the surface. In addition the outcrops beyond a mile or so from the western margin are scanty in distribution and are frequently quite unsuitable for strike and dip determinations.

The dominant strike of the beds seems to be between north-west and west-north-west, but strike directions dominantly east of north were found to hold across the central western part, and extend for nearly a mile to the highest scarp almost midway between the Roseneath and Buckey Springs Roads. This cannot be explained by simple folding since the general south-west dip still prevails further south, but it appears to be a warping across the general tilted structure. The presence of the porphyry disappearing below this seems significant but will be discussed in connection with the form of the latter intrusion. Slight folding is indicated by the surface outcrops near Roseneath. In general the beds are fairly gently dipping, the angle of dip being somewhat variable even in adjacent bands, from 10° to 30° . This variable character is probably due to current bedding.

Jointing is prominent in most of the rock types and the fine red mudstones are often shattered. Three prominent jointing directions sometimes give a sub-hexagonal pattern to the flat outcrops. Two principal directions are N. 70° W. and N. 10° W., with a third less perfect and rather variable jointing at about N. 50° E. The jointing is apparently independent of any warping since it seems fairly uniform throughout the series.

Relationship with Ordovician Rocks.

The unconformable junction between the Devonian and Ordovician strata is clearly seen at several points. On the Cathcart Road near the Reservoir, steeply-dipping Ordovician quartzites and slates forming a broad, pitching anticline are overlain by gently-dipping Devonian conglomerates and shales, the base of which is apparently irregular. Along the Buckey Springs Road gently-dipping sediments striking N. 15° E. overlie Ordovician strata whose strike is N. 10° W.

The differences in height of the junction in different parts of the area are noteworthy. This is seen most clearly near the Reservoir, where the base of the Devonian rocks against the Ordovician varies in height by 50 feet. The surface of deposition must have been highly irregular, since the feature appears to bear no relation to the Devonian structure.

Correlation.

No fossils have been found in any of these beds at Bombala, but their lithological similarity to some of the Upper Devonian rocks of the South Coast and elsewhere points to this as their probable—indeed almost certain—age. At Eden the Upper Devonian has been subdivided into three stages, and since no volcanic rocks occur within the present series, it appears to belong to the Upper or “Lambie” Stage. These beds at Eden “consist essentially of conglomerates, grits, quartzites and mudstones of shallow water origin” (Brown, 1931) which carry occasional marine fossils. They have a maximum thickness of 1,200 feet at Eden and this is also about the thickness developed at Bombala. The two series are lithologically very similar and the restriction of fossils at Eden to rare narrow bands may account for their apparent absence here. The evidences for correlation with the Lambie Stage are so strong that the Bombala Series can also be regarded as undoubtedly marine.

(c) Tertiary.

Distribution.

All rocks of Tertiary age are grouped together on the accompanying map (Plate V). The sediments and basalt are closely associated and thus “grey billy” is frequently found at the base of the basalt. Isolated patches of gravel are common, especially above the entrenched river, but are not indicated on the map. The boundary of the Tertiary sediments against the older rocks is frequently difficult to ascertain with accuracy, owing to lack of outcrops and the recent soil covering.

Of the Tertiary rocks marked, the northern area consists mainly of basalt with flat ridges of gravel and grey billy across the Coolumbooka Valley. This basalt stretches far to the north and is continuous with the widespread flows through Nimmitabel. In the southern area the basalt has been largely eroded, leaving extensive outcrops of resistant grey billy, with gravels covering most of the area. Above these, as near Lord’s Hill, ferruginous sediments are sometimes important.

Unconsolidated Sediments.

Patches of gravel, well above the height of the present river, are widely distributed through the area. They are very variable in character, some consisting of coarse rounded boulders of quartz, quartzite, etc., while others are of much finer texture and may be gritty or sandy. To the north of the Coolumbooka Bridge a gully has cut through at least 30 feet of bedded sandy grits, largely of granitic character. These must antedate the basalt in age, since, except for the topmost dark layer, no trace of basaltic material is revealed. Sometimes real granite gravels occur, almost identical with decomposed granite, as on the Bibbenluke Road past Bellview. A small area of horizontally-bedded sandstone, about 10 feet thick, caps the granite in the Coolumbooka Valley about three-quarters of a mile S.S.W. of the Coolumbooka Bridge. The maximum thickness of gravels measured was 100 feet where they are dissected by the Bombala River just within the Parish of Burnima.

Ferruginous Sediments.

Forming a ridge above the gravels near Lord's Hill is a capping of some 20 or 30 feet of horizontally-bedded ferruginous grits, sandstones and shales which contain numerous plant remains. They continue above the gravels towards Saucy Creek and form distinctive outcrops where dissected. They evidently post-dated the basalt quite considerably as they are immediately underlain by grey billy, and the high ferruginous character of the sediments is undoubtedly due to erosion of the vast covering of basalt over the land surface at that time.

They are possibly a lake deposit, and both in appearance and occurrence strongly resemble similar deposits near Cooma, Wingello, etc. "The Wingello fossil-bearing Tertiary beds", according to Jacquet (1901), "are found not only under sheets of basalt, but also over considerable areas without any protecting rock above them. They comprise beds of ferruginous shale, sandy claystones and coarse-grained sandstones." With reference to the lateritic iron ore at Wingello, Jacquet suggests that it "was formed in shallow lakes or rivers during late Tertiary times, essentially, but not entirely from basalt". These laterites have been described in a number of places in the eastern part of the State and it is noted that they nearly always overlies Tertiary beds. It is thus not unreasonable to suppose that the present highly ferruginous sediments are also the product of lake-deposition.

Grey Billy.

Silicification of the gravels in contact with the basalt has formed a resistant layer of "grey billy" which frequently remains after erosion of the igneous rock. The widespread occurrence of grey billy in this area is thus an indication of the former extent of the basalt. It occurs at heights varying from 10 feet above the river to 250 feet and usually forms low, flat outcrops. Where silicification has been more intense or erosion more rapid, the hard rock forms prominent outcrops up to 10 feet high and these may strongly resemble the tors formed by the quartz mica diorite.

In accordance with the sediments from which it is formed, the grey billy varies from fine grey, white or blue quartzites to coarse silicified conglomerates. Best outcrops occur on the Delegate Road beyond Saucy Creek, west of the Cann River Road about a mile past the Delegate turnoff, and in Macdonald's Creek north of the Cambalong Road.

On the Delegate Road opposite the Cambalong turnoff, a prominent white quartz hill stands above the level of the surrounding grey billy which is here packed with irregular fragments of quartz, and it seems that the basalt at one stage completely covered this hill.

The Basalts.

The basalts of this area are remnants of much more widespread flows undoubtedly continuous with those stretching north through Nimmitabel and Cooma. The maximum thickness attained here is 120 feet near the High Lake, and it seems apparent that the volume of lava extruded decreased towards the south.

The rocks are all basic in character, but are variable in grain size and texturally may be porphyritic or non-porphyritic, holocrystalline or hypocrystalline, massive or vesicular. The essential constituents are a basic plagioclase (labradorite), titan augite, and iron ore (probably ilmenite). Olivine may be a major constituent, usually as phenocrysts, or may be entirely absent, while differences in the titania content of the pyroxene are also reflected in thin section. Zeolites are common in the interstices and may be associated with fine apatite needles, while further north near Nimmitabel where greater thicknesses of basalt occur, the rock is riddled with large amygdulæ filled with calcite and zeolites. Occasionally coarser segregation veins occur through the normal rock and in these the ilmenite is often in parallel plates.

Tertiary History.

Detailed examination of the relative heights of the Tertiary sediments above sea level, or of their relation to the present river system, has not been made but some observations are recorded here to indicate that valuable information about the Tertiary history might be obtained on detailed study.

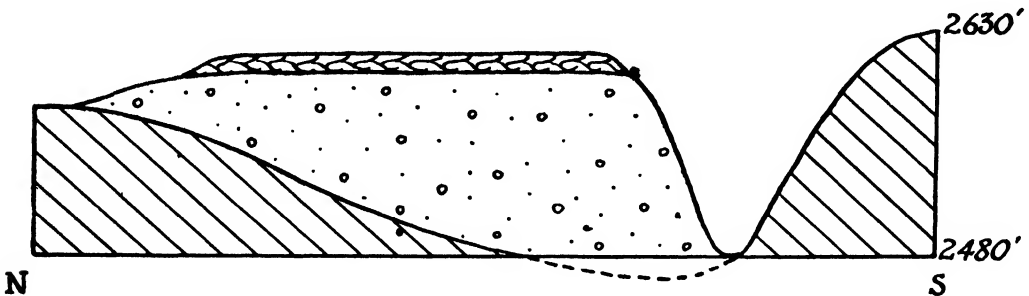


Fig. 1.—Section exposed by Bombala River at boundary of Parishes of Bombala and Burnima. The river has cut through the basalt capping, but has not yet reached the base of the Tertiary sediments. The floor of the Tertiary Valley was of slate. Scale, V : H = 1 : 3.

(1) Gravels are widespread and occur on top of the dissected Tertiary land surface up to 250 feet above the present river system. Gravels on which the town is built extend down almost to river level and rise as high as 200 feet above the river on the western side of the town. Near Burnima the river has cut through the capping of basalt and grey billy, but has not yet reached the base of the gravels, though dissection of 100 feet of gravels has been effected. (See Fig. 1.)

Saucy Creek has in places succeeded in cutting just below the base of the gravels which rise almost 100 feet above the stream.

"Granite Gravels" below the basalt (e.g. Por. 224, Parish Bombala) suggest the presence of small lakes in which the wash from the granite country was trapped.

(2) The basalt was evidently poured out over an uneven surface since great variations in its height occur. The accompanying readings are typical of the variable height of the base of the basalt. More than one flow has certainly

occurred, since bole (baked earth) has been found between flows in some parts, while springs and lakes are abundant. However, these probably represent only pulses in a single period of volcanic activity. No mineralogical characteristics have been identified with any particular flow.

Rock.	Height Above River in Feet.	River.	Locality.	Portion.	Parish.
(a) Grey Billy.	15	Bombala.	South of town.	301	Bombala.
(b) Grey Billy.	30	Bombala.	Macdonald's Ck.	37	Gecar.
(c) Basalt.	150	Bombala.	Near Burnima.	127	Bombala.
(d) Basalt.	250	Coolumbooka.	Near High Lake.	235	Bombala.

(3) The grey billy on Macdonald's Creek is surrounded by Tertiary sediments at much greater height. Moreover ferruginous sandstones, shales and grits overlie grey billy near Lord's Hill. They are therefore considerably younger than the basalt which had been eroded before their deposition. They thus appear to have been formed in a Tertiary lake, their ferruginous character being due to the basaltic nature of many of the rocks from which they were derived.

IV. INTRUSIVE ROCKS.

(a) *Plutonic.*

Three principal plutonic intrusions occur within this area. They are apparently of similar age and are thought to form part of a more extensive plutonic complex. Their general characters will be dealt with here, together with a brief account of their petrology. It is hoped to publish the results of more detailed petrological work later.

(1) *Bombala Intrusion.*

In the south-west of the area, and largely covered by Tertiary rocks, is a mass of quartz mica diorite about 15 square miles in area. It is intrusive mainly through Ordovician strata while on the eastern margin it is in contact with Devonian sediments. Except for marked variations in the height of the junction, however, their relationship is obscure, but the igneous rock is thought to intrude the sediments. It is cut off on the north by the later "Bukalong Intrusion" and a tongue of this also occurs within the eastern part of the mass. Two small outliers, one only 10 yards in length, are found at the eastern margin of the Bukalong intrusion in Portions 282 and 286, Parish Bombala, and are evidently remnants of a larger mass engulfed by the younger granite. Another mass, less than one-quarter square mile in area, intrudes the Ordovician rocks just east of here and has been called "Peadon's Intrusion". It also consists largely of quartz mica diorite which often appears to have suffered considerable contamination. At the southern end of the mass a fine biotite granite occurs and is undoubtedly related to the later Bukalong Intrusion but poor outcrops obscure the field relations.

The present terrain must be fairly close to the top of the intrusion. Small areas of Ordovician slate overlie it west of Paradise Hill, while at its junction with the Bukalong intrusion slate is found in several places.

The rocks are variable in character and appear to have been modified by contamination, especially towards the west. They are holocrystalline, with

medium or fine grainsize except for occasional large hornblendes which may attain a length of 1 cm. A slight directional structure is sometimes seen, marked principally by orientation of the hornblende crystals. Quartz is prominent among the macroscopic constituents, plagioclase (andesine) is abundant and a little irregular orthoclase may be seen. Biotite and hornblende are both present but their proportions, like those of the orthoclase and plagioclase, are variable. The fabric is hypidiomorphic granular, with subidiomorphic to idiomorphic plagioclase and hornblende. Biotite is in irregular plates and quartz and orthoclase are interstitial. Zircon, apatite and iron ore occur as accessories and a little green tourmaline is occasionally seen. Lenses of (?) prehnite are common separating the biotite cleavages.

The northern quartz mica diorite masses are undoubtedly related to the main Bombala Intrusion. Xenoliths are particularly abundant in these rocks and may attain dimensions up to two feet.

(ii) Coolumbooka Intrusion.

The typical rocks of this intrusion are granodioritic in character and fairly similar in appearance, but only the eastern tip of the mass has been examined and its full extent is unknown. A fine-grained biotite granite is also associated but will be described separately.

(a) *Granodiorite*. In general these rocks are medium-grained with some crystals attaining coarser dimensions. Visible constituents in hand-specimen are vitreous quartz, white or colourless plagioclase and pale pink orthoclase together with biotite and hornblende. The orthoclase is subordinate to plagioclase in amount and may show slight lustre mottling. The rocks are very similar in texture to those of the Bombala intrusion, but the proportions of the various minerals are different since the composition of the magma is more acid. Thus orthoclase is more abundant, plagioclase is rather more acid, and biotite is far in excess of hornblende. Apatite, zircon and iron ore are common accessories and a little interstitial calcite may be present. Several veins of tourmaline aplite have also been noted.

A porphyritic modification of the main intrusion occurs near the Parish of Coolumbooka, east of the Reservoir. Medium to coarse phenocrysts similar to the minerals of the normal rock are set in a fine-grained groundmass of more acid character, quartz and orthoclase being most abundant. Its relation to the main mass is, however, unknown since outcrops are sparse.

(b) *Biotite Granite*. A small mass of biotite granite, covering no more than an acre, outcrops near the Devonian boundary $1\frac{1}{2}$ miles north-west of the Bombala Trigonometrical Station. It is grey, medium-grained and massive with abundant, rather smoky quartz, and colourless felspar together with scattered flakes of biotite. Quartz, orthoclase, microcline and plagioclase (oligoclase) are dominant in thin section together with biotite and a little iron ore. The relation of this rock to the main granodiorite mass is not clear and although no distinct boundaries have been found between the two types, it probably represents a later intrusion, perhaps related to some of the Bukalong types. It is unfortunate that the Devonian rocks cover most of this mass.

(iii) Bukalong Intrusion.

This mass is of complex character, consisting of a number of different rock types whose field relations are by no means clear.

The southern tongue invading, and completely surrounded by the Bombala Intrusion is made up of porphyritic microgranites, aplites and coarse granites, the differences being largely textural and probably due to varying conditions of cooling, etc. These rocks weather rapidly so that fresh specimens are almost

impossible to obtain, and indeed this feature has proved a difficulty throughout most of the Bukalong mass.

The south-east part of the main intrusion is similar to this, but within the Parishes of Gecar and Pickering complex types are found. These have undoubtedly arisen by contamination but will not be discussed here. As yet it has been found impossible to separate the various rock types for field mapping.

The most normal rock appears to be a coarse biotite granite. Fresh specimens are obtainable only in railway cuttings where it is pink in colour. Normally the rock appears cream at the surface and is often stained with iron. Quartz, potash felspar and plagioclase (oligoclase) occur in comparable amounts, while biotite usually forms only a few per cent. of the rock. The potash felspar is largely of micropertthitic character but microcline may also be present. Muscovite may occur as a primary mineral in some of these rocks but is often of secondary origin associated with irregular grains of fluorite. This, together with the presence of myrmekite (Sederholm, 1916), suggests that pneumatolytic processes have been active.

A fresher and somewhat finer rock is found near the Bukalong Road in the Parish of Pickering. It is fairly extensive but its relation to the coarser mass is indefinite and in thin section it is very similar to those rocks.

West of the Bukalong Road, and stretching into the Parish of Gecar, microgranitic types are found, rich in biotite and undoubtedly not of purely igneous origin. In Portions 288 and 292, Parish Bombala two small masses of fine-grained, biotite-rich granite show a definite boundary with the coarse granite which has cooled against them. They thus represent at least an earlier phase of the Bukalong injection, if not a separate intrusion largely engulfed by the younger mass.

Large dykes of aplite and quartz, forming prominent linear features such as those across Saucy Creek near the Racecourse, are probably a late phase of the Bukalong injection while "pipes" of quartz giving bare white hills appear to represent a still later phase in the activity.

(b) *Hypabyssal.*

The most important hypabyssal rocks in this area are porphyries and rhyolites, which are divided into two groups. The first comprises a single mass south of the town, while the second group includes numerous isolated dykes which find their maximum development at Paradise Hill. For convenience they have been termed respectively the "Hospital Porphyries" and the "Paradise Porphyries".

(i) *Hospital Porphyries.*

These rocks form a mass about one-quarter square mile in area, and rather elongated in plan. They cut mainly through Ordovician rocks but to the west they are in contact with the Bombala Intrusion. A small fault seems to have displaced them along the river. On the east they are covered by the high Devonian country, and the flat cleared paddocks devoid of outcrop at the foot of these hills are probably part of this intrusion and have been mapped with it. The rocks weather very rapidly and exposures are rare. A quarry has been cut into the series near the town (Portion 28), but even here the rock is by no means fresh, although a vertical prismatic jointing may be well developed. The top of the quarry is almost coincident with the base of the Devonian rocks, and just north of this stringers of porphyry are seen penetrating these sediments. The rock has been used for surfacing the local roads but the quarry is no longer worked.

A section along the river across this mass reveals a variety of rock types. At the northern boundary of the mass on either side of the river a greenish

coloured rock of brecciated appearance is dominant. Irregular unoriented fragments of Ordovician rocks, and sometimes of aplite, may occur as inclusions in these types. The rock itself is composed of a large number of oriented fragments which give it a pronounced flow structure. These are much drawn out and seem to have been either acquired at a stage when they were not wholly solid themselves or else rendered plastic during the injection. They are probably an earlier part of the same series of injections, brecciated by continued inflow of igneous material. Scattered phenocrysts of quartz and felspar occur in the fine, recrystallized groundmass while a little garnet and occasional flakes of dark mica may be seen. Flow structure is present in most of the rocks, but shows up particularly well in the marginal types and is undoubtedly due to the high viscosity of the magma at the time of injection.

A similar feature has been described in the Loch Bà Felsite Ring Dyke at Mull, where flow brecciation in a highly viscous magma is used to explain the breccia which sometimes occurs. The Mull dyke also consists of a "beautifully flow-banded rhyolite" (Hatch and Wells, 1937, p. 348), passing in places into a slightly more crystalline "felsite". It is 100 yards to one-quarter mile in width.

Away from the northern margin, inclusions become less abundant, the rock shows less perfect flow structure in hand-specimen, and phenocrysts are more prominent and regularly distributed, with garnet and biotite increasing in relative importance. The colour of the rock is very variable and this may be due to multiplicity of injection, but is also probably influenced considerably by the degree of weathering and of deuteritic activity. No sharp junctions have been found within the mass, and on the whole the rocks are very similar under the microscope, except in the proportions of phenocrysts and groundmass. However, fragments of contemporaneous material in the rocks at the northern margin show without doubt that the mass is not the product of a single injection.

Typical rocks of the main mass contain phenocrysts of quartz and orthoclase, together with some plagioclase and mica in a hypohaline or cryptocrystalline groundmass showing strong flow banding in thin section. The flow structure is emphasized by alternate bands of very finely crystalline and of coarser material. The latter seems to have formed by shrinkage and cracking along the flow directions with the formation of parallel fibres of orthoclase and quartz around the margin of the cracks. These project into a central area filled with pale green micaceous material in radiating masses or fibres. A little crystalline albite may also occur in these areas while the quartz and orthoclase frequently form a cryptographic intergrowth, and a sub-spherulitic character is common in the wider coarse bands. Phenocrysts are less abundant in these areas.

Evidence of deuteritic activity is abundant through these rocks and albitization may be intense. Fluorite is sometimes deposited in the felspar near quartz-albite veins which are very abundant through some of the rocks. Where these veins cut across the quartz phenocrysts, they are evidenced only by a trail of minute dark specks. High power shows that these are mostly minute liquid inclusions, frequently containing gaseous bubbles which can occasionally be seen to move in the liquid.

The exact form of this intrusion presents an interesting problem. It cuts more or less linearly across the strike of the Ordovician beds along its northern margin near the river and thus seems to be dyke-like in character. Near the quarry to the north-east, however, it penetrates only the very lowest Devonian sediments, in the form of small stringers and veins along the bedding planes.

The pronounced flow structure shows that the rock was in a highly viscous state during injection so that we may picture the magma welling slowly upwards in a dyke fissure through the Ordovician strata until these suddenly give place

to gently dipping Devonian sediments. The courses which the magma may then take are twofold. Either it may continue to pass upwards through these, or else it may be squeezed laterally along the unconformity which separates the two series. Actually both processes seem to have occurred here. The magma has partly exerted its declining strength in forcing narrow stringers into the Devonian rocks possibly along tension-cracks, but the main body of magma has taken the easier course and passed along the unconformity. The vertical prismatic jointing seen in the quarry walls confirms this view since jointing usually develops at right angles to the cooling surface. Moreover the cross-warping of the Devonian strata seems to strike more or less along the direction of the feeding dyke and is undoubtedly due to the forces accompanying the rising magma.

The structure is thus that of an interformational sheet, of restricted dimensions and probably rather laccolithic in shape, together with its feeding dyke striking approximately east-west. The present case is unusual in that the horizontal extent of the mass relative to the size of the dyke is hardly of the dimensions usual to such injected masses.

(ii) Paradise Porphyries.

In contrast to the Hospital Porphyries, the rocks of the Paradise dykes are usually less decomposed and show considerably more variety of grain size and texture, etc., as well as being scattered in their distribution. They are found penetrating the slates near the margin of the plutonic masses in the south and west of the area but most are confined within the Bombala and Bukalong Intrusions. They find their maximum development at the junction of these intrusions at Paradise Hill, where they unite into a large mass standing above the general land surface. This mass alone has been drawn on the accompanying map since individual dykes, usually only of relatively narrow width, are too numerous to be plotted on this scale. Dykes continue in abundance across the river west of here and are mostly sub-parallel. This feature appears to hold for most of the series but some cross-cutting dykes are also found.

The dykes are simple or multiple and vary in width from three or four feet to 20 yards, except for the Paradise Hill mass itself, which is really a multiple dyke with a width of nearly half a mile. The strike directions of some 50 dykes have been measured, but dips usually cannot be determined. Sometimes beautiful prismatic jointing is developed across the dykes and this is particularly well seen in horizontal pavements on the western slope of Paradise Hill. The strike of the majority of the dykes lies within the limits N. 30° W. to N. 15° E. and detailed examination of the dyke system would doubtless prove fruitful. Individual dykes are difficult to trace throughout their whole length but may be as long as a mile or more.

They thus seem to constitute a "dyke swarm", but no other record of acid rocks with this structure has been found.

The series is entirely of acid character with rocks varying from non-porphyrific types showing beautiful flow structure in hand-specimen, to porphyries in which the felspar phenocrysts may be one inch or more in length. In the multiple dykes both porphyritic and non-porphyrific types may occur, the latter usually representing the first injection and reflecting a strong flow-banding.

Phenocrysts are common in most of the rocks but vary both in size and amount. Quartz and felspar are most abundant, while small well formed garnets up to one-quarter inch in diameter and similar in colour to those of the Hospital Porphyries may also occur. A little ferromagnesian material is sometimes seen in hand-specimen. Occasional inclusions, both accidental and cognate, may be present. The felspars consist of both orthoclase and acid plagioclase, the former being usually in greater abundance, but the relative proportions of

the different phenocrysts are variable throughout the series. The phenocrysts, and especially those of quartz, may be idiomorphic, but are frequently broken up and the various stages from single idiomorphic crystals to scattered rounded fragments can often be traced. (Fig. 2.)

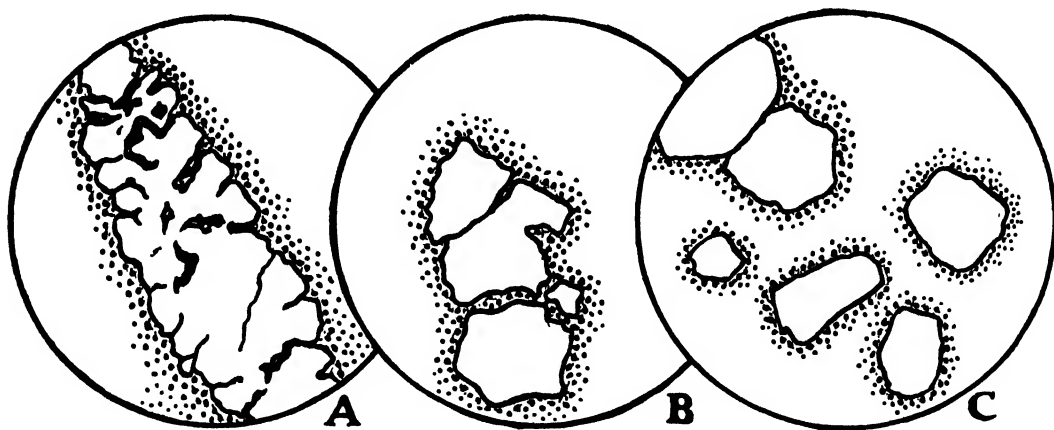


Fig. 2.—Diagram illustrating the progressive disintegration of idiomorphic quartz phenocrysts as result of attack by groundmass; and consequent presence of rounded fragments through the rock. Drawings from thin sections of Paradise Porphyries.

The orthoclase may show some albitization and the surface of the crystals is often clouded in thin section, while the plagioclase is albitic in composition. Biotite may occur with the phenocrysts but is often very altered, as in the Hospital Porphyries. Hornblende may have been present originally in a few of the rocks but is now completely altered. Occasional apatite and zircon crystals may be scattered through the rocks.

The groundmass is usually cryptocrystalline to microcrystalline with cryptographic fabric developed to varying degrees. It may be very similar to some of the Hospital Porphyries but is often coarser than these. A characteristic

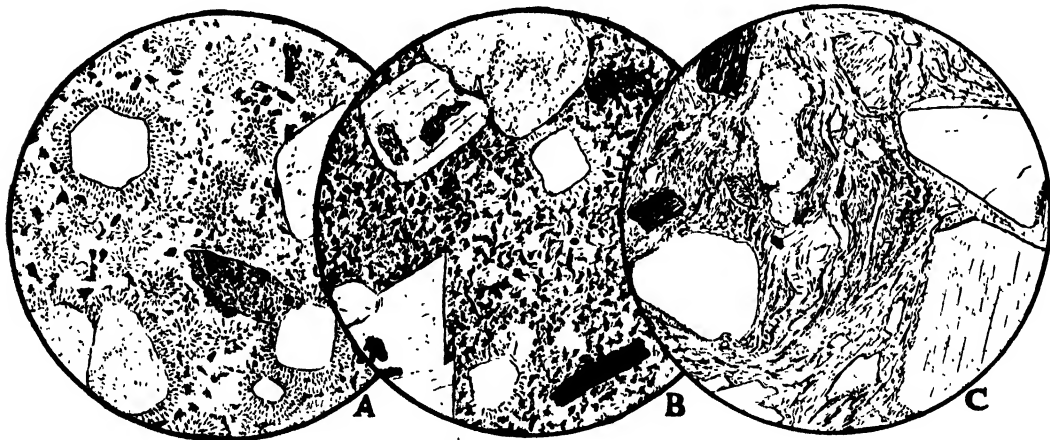


Fig. 3.—Thin sections of Paradise Porphyries illustrating different types of groundmass. A. Groundmass largely spherulitic. B. Ferromagnesian material abundant in groundmass except around quartz grains which show "reaction rim" of cryptographic quartz and felspar. C. Flow banding strongly developed by hypohyaline to cryptocrystalline groundmass.

feature is the development of a cryptographic rim devoid of dark minerals around the phenocrysts, especially around the quartz (see Fig. 3B). This is probably due to acidification of the magma immediately surrounding the grains during their disintegration, and is thus a type of reaction rim around the phenocrysts. Sometimes the groundmass acquires a sub-spherulitic character, the dark minerals being confined to the spaces between these, and the spherulites arranged along the flow direction.

(iii) Basic Dykes.

Several small basic dykes have been found and are probably related to the Tertiary volcanic activity. One of these, occurring east of Paradise Hill in Portion 32, Parish Bombala, shows phenocrysts of vitreous green olivine, and rare small black pyroxenes in a basaltic groundmass composed of tiny well formed laths of plagioclase together with irregular granules of iron ore. Occasional small white ovoid patches of zeolitic material may occur and these are lined by a zone of small projecting crystals of pyroxene. A dyke of similar rock in Portion 95, Parish Gecar, is particularly rich in pyrites. A very weathered dyke through the Ordovician slates is revealed in the railway cutting in Portion 113, Parish Bombala. It was probably also originally of basic character but now shows only a strong spheroidal weathering. This suggests that more of these basic dykes probably exist through the area but are too weathered to appear at the surface.

(c) *History of Intrusion.*

The interpretation of the intrusive history of the present igneous rocks presents some difficulties. The Bombala and Bukalong Intrusions appear to be stocks forming part of a composite bathylith. The eastern granite seems, from petrological considerations, to be part of the same plutonic complex and might be connected underground with the western mass. The abundance of xenoliths in this rock, and more especially in the Bombala Intrusion, would in the opinion of many workers indicate a proximity to the roof of the intrusion. It is evident that the successive magma injections each succeeded in enlarging the size of the bathylithic mass and did not simply enter successively into the same chamber.

Mode of Intrusion. That stoping played an important role in the emplacement of the plutonic rocks is certain, and while folding of the country rock may have accompanied the initial magma injection it seems to have been only of minor importance. Many suggestive aspects of the problems of stoping have been compiled by the Committee on Bathylith Problems under the title "Comments on Magmatic Stopping" (1935). In addition to the abundance of xenoliths, particularly in the more basic types, and the transgressive form of the intrusions, a number of observations here accord with their findings and are worthy of note.

(i) In many creek sections, tongues of acid granite are seen penetrating the Ordovician slates and in places the latter are intimately penetrated by stringers of quartz and aplite from the granite.

(ii) "Re-entrant and step-like" junctions (cf. Barrell, 1907) are seen on the south bank of the Bombala River near the Racecourse, where fine-grained offshoots of the acid Bukalong granite are seen to penetrate the Bombala mass along joint planes and represent the first stage in the rifting away of blocks of country rock.

(iii) On a larger scale parallel aplitic dykes east of Paradise Hill have penetrated along joint planes in the quartz mica diorite.

(iv) The small quartz mica diorite outliers at the eastern margin of the Bukalong granite give similar evidence of stoping. The smaller one is entirely surrounded at the surface by an aplitic phase of the acid granite and had injection proceeded for a short time longer the block, which is only about 10 yards long and a few yards wide, would have been entirely stoped away. The northern block is similarly penetrated and largely surrounded by the acid granite.

(v) The isolated block of quartz mica diorite in the southern tongue of Bukalong granite east of the Racecourse is also suggestive of stoping and may represent either a block stoped away late in the intrusive process, or else a roof pendant.

Intrusive History. The quartz mica diorite seems to have been the first of the series of injections forming the present complex, although some of the xenoliths within it suggest that it may have been preceded by a more basic magma now completely displaced. That the Bukalong Intrusion occurred after this is certain, but the position of the Coolumbooka Intrusion in the sequence is unknown as it is nowhere in contact with the other types. The general sequence of events suggests decreasing basicity as a factor in the order of intrusion and it is thus suggested that the Coolumbooka granodiorite followed the quartz mica diorite in its injection. This is corroborated by the apparent genetic relationship of the Coolumbooka rocks to the rest of the series and the usual order of intrusion in complexes of this type. The biotite granite associated with it may belong to the same stage as some of the early members of the Bukalong complex. The latter injection probably extended over a considerable period, giving rise to a number of different rock types which occasionally show an intrusive relationship to one another. The magma was, however, frequently modified by contamination with the country rocks. The aplites were probably in part contemporaneous with the acid injections, representing the initial stages of injection along joints, etc.

The dying stages of the diastrophism were evidently marked by the more or less simultaneous injection of the Hospital Porphyries and Paradise complex, although the relation of the former to the intrusive series is not certain. The final stages were marked by dykes of quartz and aplite such as those across the Racecourse and on Saucy Creek, and by great masses of quartz forming dykes or pipes either within the granite near its margin, or penetrating the country rocks, when the granite can safely be assumed to lie fairly close below the land-surface.

Age. The age of the intrusion is not definite. Small aplite offshoots penetrate the Devonian sediments in the southern part of the Coolumbooka granite, and a consideration of the contour of the base of the Devonian rocks, which varies considerably within a few hundred yards near the Reservoir, also suggests an intrusive relationship between them, although the Ordovician-Devonian boundary nearby is also quite irregular. The general lack of metamorphism in the Devonian rocks is another factor which has not yet found satisfactory explanation. A few sediments carrying biotite occur near the aplite offshoots in Portion 93, but this mineral seems to be definitely of primary origin and is probably due to the tuffaceous character of the rock. Thin section shows that even the shale fragments in these rocks have not developed biotite, and while a few show a little recrystallization, many are unaffected. On the other hand contact effects in the Ordovician slates have never reached a high metamorphic grade either. It may be significant that some bands in the series are highly siliceous but unless some obscure agency has enabled the transfer of heat through to these highly siliceous bands—a highly improbable and unsatisfactory explanation—the problem must be left open and the Coolumbooka Series assumed to be younger than the Devonian sediments.

The relation of the Hospital Porphyries to the Paradise Intrusions is also important in determining their age. The character of the rocks is so similar, however, that there seems little doubt of their consanguinity, the Hospital types having suffered more deuteric activity, possibly because they were intruded more or less simultaneously and are not isolated.

The junction between the Hospital Porphyries and the quartz mica diorite near the river is unfortunately covered by soil and gravel, but occasional inclusions of aplite in the Porphyries suggest that they were intruded after the plutonic rocks were emplaced. If their consanguinity with the Paradise Porphyries is assumed then it is evident that the Hospital Porphyries post-date the quartz mica diorite. They are definitely intrusive into the Devonian sediments and hence the western intrusive rocks at least are post-Devonian. If the Coolumbooka Intrusion be interpolated into its natural place in the series, it is then also post-Devonian, and the series is assumed to belong to the diastrophism which terminated the Devonian period and termed by Sussmilch (1914) the Kanimbla epoch. This is the age ascribed to these rocks in a general way by Browne (1929, p. 24).

V. PHYSIOGRAPHY.

The mature topography between Nimmitabel and the Victorian border beyond Delegate has been considerably influenced by the nature of the country rocks. This, together with the extensive occurrence of basalt and of Tertiary sediments, gives to the area a rare topographic interest. A brief outline of some aspects of the physiography of the district will be given here.

(a) *Topography.*

The town of Bombala, with a height of 2,313 feet above sea level, lies in the southern part of what Sussmilch (1909) termed the Yass-Canberra or Monaro peneplain. Some ten miles to the east this plain descends steeply down the Coastal Range to the Coastal Plain, which has a width here of about 30 miles. The descent is of the order of 2,000 feet and is for the most part inaccessible. To the west the mature countryside carries for some distance till it gives place to the high mountains known as the Southern Alps. These include Mt. Kosciusko (over 7,300 feet), the highest point in Australia, at a distance of 65 miles direct from Bombala, and during the prolonged winter months the snow-capped Alpine ridges can be seen from many of the Bombala hilltops.

The eastern part of the area shows well the structural influence of the Devonian rocks in its evolution. Gently inclined dip-slopes are thus a common sight against the eastern skyline. The jointing in these rocks has also caused the development of cliff-like scarps at the western margin of the more massive strata. The red shales on the other hand have weathered much more readily and tend to form smooth, depressed areas among the more resistant grits.

The relief of the eastern zone is greater than that of the surrounding plain, the height rising to 3,144 feet at the Bombala Trigonometrical Station. Across the town to the west the relief is not so marked, the highest point being at "Paradise Hill", some 400 feet above the river and about 2,700 feet above sea level. This feature is due entirely to the resistant character of the rhyolites and porphyries of which it is composed relative to the surrounding granites. The "Hospital Porphyries" near the town, by contrast, have weathered more readily and do not rise above the general level of the surrounding slates.

The granite country, like that of the slates, has an undulating contour except where dissection by the river has caused the development of steep valley walls in the slate country. In the nature of their outcrops, however, as well as in their vegetation the principal plutonic rock-types are readily separable in the field. The coarse Bukalong granite weathers rapidly forming low flat outcrops

with little soil covering so that as a rule this country is rather poor. The finer "Bukalong" types are more resistant and may form prominent rugged outcrops. The rocks of the "Bombala" intrusion, on the other hand, weather less rapidly and form the characteristic rounded tors at the surface. The soil thus formed is also richer, possibly because of its higher iron content, and bears more profuse vegetation. This difference is also reflected in the fact that the areas of more basic rock have generally been cleared earlier than the acid types, which in places are still uncleared. The eastern granite from which the Coolumbooka River has carved its valley forms low, cleared undulating hills capped on the west by flat-topped basalt scarps and on the south by the rough Devonian hills.

Extensive Tertiary sediments across the southern part of the area form a flat-topped unit into which the streams are now cutting with considerable effect.

(b) The Drainage System.

The whole of the Monaro peneplain south of the main "Monaro" Divide which passes through Nimmitabel in a north-westerly direction, forms part of the drainage system of the Snowy River.

The Bombala River has its headwaters near the Brown Mountain and flows southward in a meandering course through Bibbenluke, being joined by the Coolumbooka River below the Bombala Reservoir. It meanders south through the Parish of Bombala to below the town, where it swings back in a north-westerly direction and follows a fairly straight course till it is joined by Brugolong Creek, where it again changes direction towards the south-west and joins the Delegate River near Quidong.

Some indication of the circuitous course taken by the river can be gleaned when it is realized that in a direct southerly distance of four miles from where the river enters from the Parish of Burnima to where it swings westward below the town, the present river course covers some eleven miles. The average gradient throughout this stretch is about 15 feet per mile.

The dissection of the land surface is, however, much greater than would be expected in a stream of such mature character, and this may be taken as evidence of its rejuvenation. The maximum dissection is usually about 150 feet. The amount of water which the streams carry varies considerably with the season. After heavy rains upstream the Bombala River often rises 30 feet, while even in the driest season it is never empty because of the large number of springs in the basaltic country to the north.

VI. SUMMARY.

A plutonic complex of Kanimbla age is intrusive through Upper Ordovician slates and Upper Devonian red-beds of Lambie Type. Three main intrusions occur, consisting of quartz mica diorite, granodiorite and biotite granite respectively. Contamination has modified some of these but is not discussed in detail here. Associated with these plutonic rocks is a very interesting dyke swarm of highly acid character and frequently carrying garnet. Tertiary sediments and basalt cover much of the area and give promise of useful results on detailed study.

VII. ACKNOWLEDGEMENTS.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART X. THE OXIDATION OF CÆSIUM HEXACHLORO-RHODATE III TO CÆSIUM HEXACHLORO-RHODATE IV.

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It is well known that in most of its compounds rhodium is trivalent, but as the centre member of the triad containing cobalt and iridium it might also be expected to display the bivalency and tetravalency characteristic of these elements. The existence of simple rhodium II salts is doubtful (Dwyer and Nyholm, 1941), despite the preparation of deeply coloured impure salts by the authors, and recent experiments indicate that the simple ion Rh^{++} undergoes disproportionation to trivalent rhodium and the free metal. A number of complex salts of rhodium II have been prepared, however (Dwyer and Nyholm, 1941, 1942, 1943).

The only compound of tetravalent rhodium described in the literature is the green hydrated dioxide $\text{RhO}_2 \cdot x\text{H}_2\text{O}$, originally obtained by the chlorination of sodium rhodate III, when it appeared as a precipitate, leaving a violet blue solution, which was claimed to contain hexavalent rhodium as sodium rhodate VI, Na_2RhO_4 (Claus, 1860). Wohler and Ewald (1931) showed that the oxide prepared by Claus had an oxygen content between Rh_2O_3 and RhO_2 and succeeded in preparing the dark green hydrated oxide in purer form by the anodic oxidation of sodium rhodate III. It was noted that the oxide dissolved in hydrochloric acid with the liberation of chlorine and the formation of the usual red rhodium III chloride, but the evidence did not distinguish unequivocally between a true quadrivalent oxide and a peroxide. Ruff and Ascher (1929), by the fluorination of rhodium sponge, obtained RhF_3 , as well as small amounts of a red-brown sublimate with a higher fluorine content but were unable to decide whether the substance was a tetrafluoride or a pentafluoride. Grube and Gu (1937) made an extensive study of the anodic oxidation of rhodium III salts in sulphuric, nitric and perchloric acids and found that the oxidation yielded first a green solution, which finally became violet. From potentiometric titrations of the oxidized solutions it was concluded that the green solutions contained quadrivalent rhodium and the violet hexavalent rhodium, present probably as the acid H_2RhO_4 . Evidence was adduced to show that the quadrivalent compound underwent disproportionation: $3\text{Rh}^{\text{IV}} \longrightarrow \text{Rh}^{\text{VI}} + 2\text{Rh}^{\text{III}}$. The redox potential of the quadrivalent/trivalent system was found to be approximately 1.40 volts. Studies of this system now being carried out indicate that this potential is actually somewhat higher. Grube and Auteriet (1938) failed to oxidize chloropentammine rhodium III perchlorate, potassium hexacyanorhodate III, or rhodium trifluoride in hydrofluoric acid. In the latter oxidation a green precipitate of (probably) the hydrated oxide was obtained at the anode.

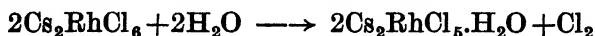
The most characteristic and stable compounds of most metals in the quadrivalent state are the alkali metal hexahalogenates R_2MX_6 , which form an

isomorphous series crystallizing in the cubic system, and the isolation of a complex of this type, it was felt would provide the best evidence for the existence of quadrivalent rhodium. Since the chloro compounds are the best defined of these complexes, the preparation of the compounds R_2RhCl_6 has been attempted.

Although the potential of the Rh^{IV}/Rh^{III} system is above the potential of the chlorine/chloride electrode, it can be deduced from the ordinary redox equation that if the concentration of quadrivalent rhodium is kept sufficiently low by the formation of an insoluble complex that trivalent rhodium can be oxidized by chlorine, i.e. in the presence of chloride ions. Among the platinum metals the solubility of the chloro complexes decrease notably as the size of the cation R is increased, and normally the caesium compound is highly insoluble.

In the initial series of experiments cold solutions of rhodium trichloride in the presence of caesium chloride were treated with chlorine or oxidized anodically. Traces of a green insoluble material with pronounced oxidizing properties were isolated, but the yields were extremely low, and the product was contaminated with a reddish non-oxidizing material. The amount of the green substance could be increased by the addition of hydrochloric acid and boiling just prior to the oxidation. Rhodium trichloride is well known to yield three types of complex with alkali halides: R_3RhCl_6 ; $R_2RhCl_5 \cdot H_2O$ and $R_2RhCl_4 \cdot 2H_2O$, and in solution in the presence of chloride ions there appears to be an equilibrium between the ions $RhCl_6'''$, $RhCl_5 \cdot H_2O''$ and $RhCl_4 \cdot 2H_2O'$. The beneficial effect of hydrochloric acid is thus due probably to the movement of the equilibrium to favour the ion $RhCl_6'''$ which appears to be the ion capable of oxidation. However, it was found that a large excess of chloride ion or hydrochloric acid completely inhibited the formation of the green substance. The oxidizing potential of chlorine falls with increasing chloride ion concentration, and apparently, in the presence of sufficient chloride ion to stabilize the $RhCl_6'''$ ion, the available potential is too low to permit oxidation.

The difficulty was finally overcome by isolating the $RhCl_6'''$ ion as the caesium salt Cs_3RhCl_6 in the form of a very fine precipitate, suspending it in ice water in the presence of a little caesium chloride and immediately oxidizing with ceric nitrate, when it was transformed quantitatively to the very sparingly soluble, green, compound caesium hexachlororhodate IV, Cs_2RhCl_6 . The compound decomposed rapidly in the presence of water with the liberation of chlorine and the formation of the reddish crystalline caesium aquo pentachlororhodate III, $Cs_2RhCl_5 \cdot H_2O$.



It was instantly reduced with a colour change to rose red by bromide ions, sulphurous acid, ferrous sulphate or stannous chloride. Owing to the rapid decomposition in the presence of water it was not possible to dry the substance sufficiently rapidly to obtain samples for analysis, and the analysis was carried out on the wet material and the composition deduced from the ratio of the constituents.

The constitution was confirmed by X-ray powder photographs on very small samples dried rapidly in vacuum over phosphorus pentoxide. The perfectly dry material is stable. The substance was face centred cubic, isomorphous with ammonium chloroplatinate. The length of the side of the unit cube 10.2 \AA . is very close to value for caesium hexachloroplatinate. From the structure parameter, $u = 0.23 \pm 0.01$, the distance $Rh^{IV}-Cl$ is 2.3 \AA .

Attempts to oxidize potassium, ammonium or rubidium hexachlororhodate III were unsuccessful.

EXPERIMENTAL.

Cæsium Hexachloro-Rhodate IV. Anhydrous sodium hexachlororhodate III, prepared by fusion of rhodium black with sodium chloride in chlorine (0.5 g.), was dissolved in water (7 ml.), cooled to 0° and rapidly brought into solution. Traces of rhodium metal were removed by centrifuging in a tube cooled in ice. (If the sodium salt is allowed to stand or become warm, it is rapidly transformed to the aquo-pentachloro compound.) Cæsium chloride (1.0 g.) was added immediately, and the mixture shaken, when a pale rose-coloured precipitate of the cæsium compound resulted. The precipitate was centrifuged to the bottom of the tube and the supernatant liquid removed. A further 0.2 g. of cæsium chloride was added to the precipitate, followed by 12.5 ml. of ice cold ceric nitrate (0.1 N.) in nitric acid (1.1 N.) saturated with chlorine. On shaking, the mixture became a deep bluish green. This precipitate was centrifuged, the mother liquor removed, and fresh ice cold ceric nitrate added. This was repeated again, and the precipitate washed twice with ice cold nitric acid 0.1 N. Thin smears of the green compound were rapidly dried in vacuum over phosphorus pentoxide for the X ray examination, and the remainder of the material immediately used for the analysis.

The oxidation of cæsium hexachlororhodate III could be effected with potassium permanganate provided nitric acid stronger than 3 N. was mixed with it, but potassium dichromate was ineffective.

Analysis of Cæsium Hexachloro-Rhodate.

(1) *Ratio of Total Chlorine to Oxidizing Chlorine.* The material in the centrifuge tube was immediately treated with an excess of approximately 0.1 N. ferrous sulphate, and the excess determined by potentiometric titration with sodium permanganate. At the end of the titration a few drops of ferrous sulphate were added to prevent loss of the chlorine by reaction with the permanganate. The solution was then made up to 100 c.c., and 25 c.c. were treated with excess of 0.05 N. silver nitrate and a little concentrated nitric acid. The mixture was heated to precipitate the silver chloride completely, then diluted with water, and the excess silver nitrate determined with standard thiocyanate with ferric alum as an indicator.

Found: Total chlorine = 0.01575 g.; oxidizing chlorine = 0.00244 g. The ratio is thus 6.4/1.

(Although this is higher than the theoretical value 6.0/1, it should be noted that the ratio is increased by traces of chlorine not washed out during the preparation as well as direct loss of chlorine from the oxidized substance.)

(2) *Ratio of Rhodium to Total Chlorine.* A portion of the solution reduced with ferrous sulphate was treated with pure zinc dust and boiled to precipitate rhodium metal. After treatment with sulphuric acid, the metal was weighed.

Found: Rh = 0.0078 g.; Cl = 0.01575 g. Rh/Cl = 1/5.9. Calculated Rh/Cl = 1/6.

(3) *Ratio of Cæsium to Chlorine.* A portion of the solution reduced with ferrous sulphate was heated to boiling and made alkaline with sodium hydroxide. Drops of hydrogen peroxide were then added to complete the precipitation of ferric, rhodium and manganese hydroxides, and the precipitate removed. The filtrate was concentrated and the cæsium precipitated with chloroplatinic acid in the presence of alcohol.

Found: Cs₂PtCl₆ = 0.0494 g. or 0.0195 g. Cs; Cl = 0.01575 g. Cl/Cs = 3.02/1. Calculated: Cl/Cs = 3.0/1.

The Decomposition of Cæsium Hexachloro-Rhodate IV in Water.

Some of the green material was allowed to stand in contact with distilled water for two days. Chlorine was evolved and the material passed partly into solution and part gave brownish red prisms. The red solution on evaporation also gave reddish brown prisms. Analysis for chlorine and rhodium showed the substance to be cæsium aquo-pentachloro-rhodate III.

Found: Cl = 31.7%, 31.4%; Rh = 18.3%. Calculated for Cs₂RhCl₅.H₂O: Cl = 31.47; Rh = 18.24%.

The Crystal Structure of Cæsium Hexachloro-Rhodate IV.

X-ray diffraction photographs of the following powder specimens were taken: (I) The starting material, cæsium hexachloro rhodate III, $\text{Cs}_2\text{RhCl}_6 \cdot \text{H}_2\text{O}$; (II) the green powder, cæsium hexachloro rhodate IV, Cs_2RhCl_6 ; (III) the decomposition product, cæsium aquo pentachloro rhodate III. Photographs were taken in a 9 cm. camera and specimens I and II in a 19 cm. camera. With specimens I and III the material was placed on a glass fibre, but II was packed into thin celluloid tubes and sealed. Exposure times with filtered Cu radiation from a G.E. diffraction tube were 1 hr. in the 9 cm. camera and 4 hrs. in the 19 cm. camera. The green material did not appear to decompose during the exposures.

TABLE I.

Calculated and Observed Intensities of Reflections for Values of u between 0.20 and 0.25 Å. for Cs_2RhCl_6 ; Space Group O_h^5 ($Fm\bar{3}m$); $a=10.2$ Å.

Line N.*	Calculated Intensities. $u=$						Observed Intensities. Film		
	0.25	0.24	0.23	0.22	0.21	0.20	1	2	3
3	5.2	6.1	7.0	7.6	8.2	8.8	5	5	5
4	2.6	2.6	2.5	2.4	2.3	2.1	—	—	v.w.
8	9.6	9.6	9.7	9.9	10.1	10.5	10	10	10
11	4.0	3.8	3.7	3.5	3.5	3.6	—	2	2 to 3
12	7.7	7.6	7.5	7.4	7.1	6.9	8	8	8
16	8.4	8.4	8.2	8.1	7.9	7.6	9	9	9
19	2.8	2.1	1.6	1.1	0.7	0.4	—	—	1
20	1.5	1.6	1.8	1.9	2.1	2.3	—	—	1
24	6.2	6.2	6.1	6.0	5.9	5.8	6	6	7
27	2.3	2.9	3.3	3.7	4.1	4.3	2	2	3
32	6.8	6.7	6.6	6.3	6.0	5.8	7	7	7.5
35	2.3	2.6	2.8	3.0	3.1	2.0	2	—	3
36	1.5	1.7	1.8	2.0	2.3	2.65	—	—	1
40	4.3	4.4	4.6	4.9	5.3	5.7	4	4	4
43	0	0	0.2	0.5	0.8	0.9	—	—	—
44	4.1	4.0	3.8	3.4	3.0	2.6	3.5	<3.5	4
48	3.9	3.9	3.7	3.5	3.2	3.0	3.5	>3.5	4
51	1.7	2.0	2.5	2.7	2.9	3.1	1	—	2.5
52	0.75	0.7	0.7	0.6	0.5	0.4	—	—	<1
56	4.4	4.4	4.6	4.9	5.0	5.3	5	5	5

* $N = h^2 + k^2 + l^2$.

Specimen I gave a diffraction pattern which was not cubic; II gave a simple pattern with reflections agreeing with a face centred cubic lattice; III gave a complex diffraction pattern. On some of the photographs of II one or two reflections appeared which were additional to those expected from the cubic system, but these lines always coincided with the most intense lines of the decomposition product. From the diffraction data a value of the lattice parameter a was found to be 10.2 Å. This constant could not be determined more accurately owing to the difficulty of indexing the high angle lines.

An examination of the indices of the reflections present indicated that the space group O_h^5 ($Fm\bar{3}m$) was a possible one and that the substance could therefore be isomorphous with ammonium chloroplatinate. Density determinations could not be made on the material, but if the assumption of isomorphism is correct there would be four molecules per unit cell. With these assumptions and taking $a=10.2$ Å. the expected intensities of reflections of the powder reflection lines were calculated for a structure parameter u lying between 0.17 and 0.25. These intensities were then compared with a visual estimate of the intensities of the lines on the photographs. Table I gives the comparison of the calculated and observed intensities for different values of u for some

of the lines examined. The intensities of the higher angle lines are more sensitive to changes of u but unfortunately these lines were very faint. The parameter u would appear to lie between 0.21 and 0.25, the most likely value being 0.23 ± 0.01 .

The green material thus gave diffraction data which agreed closely with that of a substance having the formula Cs_2RhCl_6 , space group O_h^5 , isomorphous with $(\text{NH}_4)_2\text{PtCl}_6$, with four molecules per unit cell. From the values of the lattice and structure parameters the $\text{Rh}^{\text{IV}}-\text{Cl}$ distance is 2.3 Å.

Table II gives a comparison of lattice and structure parameters for other substances of this type.

TABLE II.

Comparison of Lattice Parameters, a , and Structure Parameters, u , for Crystals with Structure of Ammonium Chloroplatinate Type.

Crystal.	a (Å).	u .	R-X Distance (Å).
$(\text{NH}_4)_2\text{PtCl}_6^*$..	9.84	0.207	2.36
$\text{Cs}_2\text{GeF}_6^*$..	8.99	0.20	1.80
$\text{K}_2\text{PtCl}_6^*$..	9.73	0.240	2.33
$\text{K}_2\text{SnCl}_6^*$..	9.93	0.245	2.43
$(\text{NH}_4)_2\text{PbCl}_6^*$..	10.14	0.23	2.33
$(\text{NH}_4)_2\text{SiF}_6^*$..	8.38	0.205	1.72
$(\text{NH}_4)_2\text{SnCl}_6^*$..	10.05	0.245	2.45
Cs_2RhCl_6 ..	10.2	0.22 to 0.24	2.20 to 2.4

* Values taken from Wyckoff, "The Structure of Crystals", The Chemical Catalogue Co., New York, 1931.

SUMMARY.

Cæsium hexachloro rhodate III has been found to react with ceric nitrate in dilute nitric acid to yield a green insoluble material, cæsium hexachloro-rhodate IV. This compound has been examined by X-ray diffraction and found to be isomorphous with ammonium chloroplatinate, thus demonstrating that it is a compound of quadrivalent rhodium.

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THE CHEMISTRY OF OSMIUM.

PART III. COMPLEXES OF TERTIARY ARSINES WITH BIVALENT AND TRIVALENT OSMIUM HALIDES.

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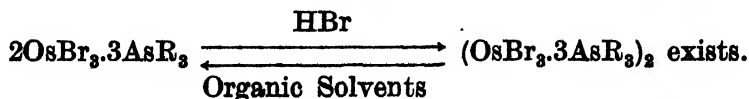
and B. T. TYSON.

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Very few complex compounds of bivalent or trivalent osmium have been described in the literature. This is due no doubt to the fact that both valency states have powerful reducing properties. The potential of the quadrivalent/trivalent osmium couple in hydrobromic and hydrochloric acids is 0.452 volt (Dwyer, McKenzie and Nyholm, 1945; Dwyer, Humpoletz and Nyholm, 1946), whilst the estimated potential of the trivalent/bivalent couple is probably as low as -0.2 volt. The stabilization of the powerfully reducing bivalent states of iridium and rhodium with tertiary arsines (Dwyer and Nyholm, 1941, 1942, 1943), however, suggested that stable complexes of bivalent and trivalent osmium might be obtained in a similar manner.

Quadrivalent osmium in the form of the hexahalogenates, R_2OsX_6 , failed to yield complexes with either tertiary arsines, tributyl phosphine, or diethyl sulphide. In the presence of halogen acids, tributyl phosphine acted as a base and salts of the type $(Bu_3P.H)_2OsX_6$ were isolated. The salts were sufficiently stable to be recrystallized from alcohol. This is surprising in view of the weakly basic nature of the alkyl phosphines, but salts of this type are not unique, for Burrows and Turner (1921) showed that tertiary arsines, which are even less basic, may yield salts of acids with large anions.

When the hexahalogeno osmates were refluxed with tertiary arsines for some time, the solutions changed colour due to reduction and the resulting trivalent osmium compound coordinated with excess of arsine to yield chloro and bromo compounds of the type $OsX_3.3AsR_3$. These compounds crystallized well in pink or deep red needles, with sharp melting points, and were easily soluble in the usual organic solvents. The compounds failed to react with cold alcoholic silver nitrate, but on heating a precipitate of silver metal and silver halide resulted. The molecular weight of the tris-dimethylphenylarsine bromo compound was normal in benzene and the substances are accordingly the usual simple hexavalent compounds, the analogues of the arsine complexes with trivalent ruthenium (Dwyer and Nyholm, 1946), iridium and rhodium. Like the rhodium compounds, tris-dimethylphenylarsine tribromo-osmium was found to exist in two forms. Although the two forms were monomeric in benzene, the evidence suggests that the compounds are not isomeric, since the high melting form is transformed into the lower melting form simply by dissolution in benzene, whilst the reverse change can be effected by solution of the lower melting form in alcohol in the presence of hydrobromic acid. It is probable that an equilibrium



It was not possible to determine the constitution of the proposed dimer, but three formulations are feasible: $[\text{Os}(\text{AsR}_3)_6][\text{OsBr}_6]$; $[\text{Os}(\text{AsR}_3)_5\text{Br}][\text{OsBr}_5(\text{AsR}_3)]$; and $[\text{Os}(\text{AsR}_3)_4\text{Br}_2][\text{OsBr}_4(\text{AsR}_3)_2]$.

It was not possible to isolate complexes of osmium tri-iodide and arsines, as in all cases the reduction proceeded to the bivalent state.

As with rhodium, iridium and ruthenium, the trivalent complexes were reducible with hot hypophosphorous acid to the paler coloured bivalent osmium compounds. The chloro and bromo compounds were of the form $\text{OsX}_2 \cdot 4\text{AsR}_3$, and reduced alcoholic silver nitrate to the metal at room temperature. The deeply coloured iodo complexes, however, which were obtained simply by boiling the trivalent chloro or bromo compounds with hydriodic acid, were of the form $\text{OsI}_2 \cdot 3\text{AsR}_3$, and like the rhodium II compounds probably contain iodine bridges to maintain hexacovalency. Attempts to prepare tetrakis arsine iodo compounds were fruitless.

The analysis of these osmium compounds was unsatisfactory in that a successful method of estimating either arsenic or osmium in the presence of each other and organic matter could not be devised. Analyses for carbon and hydrogen were also unreliable owing to the attack of osmium tetroxide formed during the combustion on the tap grease of the absorption tubes. The compounds were thus analysed only for halogen by the distillation method described in previous papers.

Attempts to prepare complexes of bivalent or trivalent osmium with tributyl phosphine or diethyl sulphide were unsuccessful.

EXPERIMENTAL.

Tris-Diphenylmethylarsine-Tri-Bromo-Osmium. Potassium hexabromosmate (0.5 g.) was dissolved in hydrobromic acid (30 mls. of 3 N.), and heated to 80° C., and diphenylmethyl arsine (0.55 g., $3\frac{1}{2}$ mols.) dissolved in hot alcohol (30 ml.) added. The mixture was refluxed for fifteen minutes, when the dark brownish red solution lightened to red, and a red crystalline precipitate commenced to form. The mixture was diluted with a little water and cooled. The impure material recrystallized from acetone melted at 176–178° and gave Br=14.3%. (Pure compound requires Br=20.65%.) This material was recrystallized twice from acetone, and finally fractionally precipitated from acetone with water. The least soluble fractions gave bright red needles, m.p. 205° and analysed correctly for the halogen. The substance was sparingly soluble in alcohol, but easily soluble in benzene and chloroform. An alcoholic solution heated with alcoholic silver nitrate gave a black precipitate of silver metal and silver bromide.

Found: Br=20.8; 20.9%. Mol. wt. cryoscopic in benzene, 1230. Calculated for $\text{OsBr}_3 \cdot 3\text{Ph}_2\text{MeAs}$: Br=20.65%; mol. wt. 1162.

Tris-Dimethylphenylarsine-Tri-Bromo-Osmium, Low Melting Form. The preparation was repeated as above, substituting dimethylphenylarsine, and heating the mixture for only 5–6 minutes. The red crystalline precipitate formed on dilution with water was heated with alcohol when part dissolved. The alcoholic solution was then fractionally precipitated with water. The middle fraction gave red needles, m.p. 163°, easily soluble in alcohol, acetone and benzene. The molecular weight of the substance in benzene was normal, and the original material was obtained from the benzene after evaporation at room temperature. A solution of the substance in alcohol containing 5% of concentrated hydrobromic acid crystallized overnight to yield red needles and plates m.p. 173° of the higher melting form.

Found; Br=24.3%; mol. wt. 962. Calculated for $\text{OsBr}_3 \cdot 3\text{PhMe}_2\text{As}$: Br=24.6%; mol. wt. 976:

Tris-Dimethylphenylarsine-Tri-Bromo-Osmium, High Melting Form. The portion of the preparation above which was insoluble in alcohol was dissolved in hot acetone and fractionally precipitated with water. The least soluble fraction gave red needles and plates, m.p. 173°, from aqueous acetone. The molecular weight in benzene was normal, but the material recovered

from the benzene by evaporation at room temperature melted at 163° and was soluble in alcohol. During the initial preparation of the substance larger yields can be obtained at the expense of the lower melting form by refluxing for a longer time.

Found: Br=24.4%; mol. wt. 970. Calculated for $\text{OsBr}_2 \cdot 3\text{PhMe}_2\text{As}$: Br=24.6%; mol. wt. 976.

Tris-Diphenylmethylarsine-Tri-Chloro-Osmium. Potassium hexachlorosmate (0.5 g.) in normal hydrochloric acid was heated to 80°C . and treated with diphenylmethylarsine (0.9 g., $3\frac{1}{2}$ mols.) in hot alcohol (30 ml.) and refluxed. The initially cloudy yellow solution became reddish after 20–25 minutes, and was diluted with water and cooled. The orange red oil which separated was treated with petroleum ether and allowed to stand overnight. The resulting pink solid was crystallized several times from dilute aqueous alcohol containing a little hydrochloric acid and gave finally pink needles, m.p. 120° . The substance was similar in properties to the bromide. Very poor yields were obtained in the preparation, and much potassium hexachlorosmate was recovered each time.

Found: Cl=10.4%. Calculated for $\text{OsCl}_3 \cdot 3\text{Ph}_2\text{MeAs}$: Cl=10.35%.

Tris-Dimethylphenylarsine-Trichloro-Osmium. Prepared as above in better yields, this substance crystallized well in pinkish-orange needles, m.p. 185° .

Found: Cl=12.7%. Calculated for $\text{OsCl}_3 \cdot 3\text{PhMe}_2\text{As}$: Cl=12.59%.

Tetrakis-Diphenylmethylarsine-Dichloro-Osmium. Potassium hexachlorosmate (0.4 g.) in 2 N. hydrochloric acid (30 mls.) was treated with diphenylmethylarsine (0.88 g., $4\frac{1}{2}$ mols.) in alcohol (20 mls.) and 30% hypophosphorous acid (2 ml.) added. The mixture, on heating, became reddish due to the formation of the osmium III complex, and then yellow as the reduction proceeded. The mixture was diluted considerably with water, and shaken with petroleum ether when a yellow sticky mass resulted. This was crystallized several times from dilute aqueous alcohol to give a pale yellow microcrystalline powder, m.p. 113° . The substance was very soluble in all organic solvents except petroleum ether. An alcoholic solution reduced alcoholic silver nitrate to the metal at room temperature.

Found: Cl=5.6%. Calculated for $\text{OsCl}_2 \cdot 4\text{Ph}_2\text{MeAs}$: Cl=5.7%.

Tetrakis-Dimethylphenylarsine-Dichloro-Osmium. Prepared in a similar manner to the compound above, the substance was a pale yellow micro-crystalline powder, m.p. $133\text{--}135^{\circ}$.

Found: Cl=7.1%. Calculated for $\text{OsCl}_2 \cdot 3\text{PhMe}_2\text{As}$: Cl=7.17%.

Tetrakis-Diphenylmethylarsine-Dibromo-Osmium. This was prepared in a similar manner to the chloro compound above, except that the reduction was stopped as soon as the red colour of the osmium III compound was discharged. The yields from various preparations were poor, and if the reduction was carried too far small amounts only of an unknown substance containing a low proportion of bromine and (probably) hypophosphite were obtained. After repeated crystallization from aqueous alcohol the substance was obtained as a brownish yellow powder, m.p. 100° .

Found: Br=11.9%. Calculated for $\text{OsBr}_2 \cdot 4\text{Ph}_2\text{MeAs}$: Br=12.05%.

Tetrakis-Dimethylphenylarsine-Dibromo-Osmium. Prepared in poor yield as the bromo compound above the substance was a brownish yellow powder, m.p. 131° .

Found: Br=14.0%. Calculated for $\text{OsBr}_2 \cdot 4\text{PhMe}_2\text{As}$: Br=14.84%.

Di-Iodo-Hexakis-Diphenylmethylarsine-Diodo-Diosmium. During attempts to prepare complexes of osmium tri-iodide by treatment of potassium hexachloro or hexabromo osmate with hydriodic acid and diphenylmethyl arsine it was noted that a mixture of compounds resulted as well as black osmium iodide. Finally an effort was made to replace the chlorine or bromine in the tris chloro or bromo arsine complexes with iodine by refluxing with purified hydriodic acid, in acetone solution. The result was a purplish black crystalline compound, which was crystallized fractionally from acetone. The least soluble fractions gave the correct analysis for a bivalent osmium complex with three coordinated arsine molecules, but the most soluble fraction was greenish in colour and gave I=32.6% ($\text{OsI}_2 \cdot 3\text{Ph}_2\text{MeAs}$ requires I=29.2%). Over a number of preparations the green substance gave values of iodine varying from 30% to 33%, and all efforts to purify or formulate the substance have failed. The dark purplish substance after many

crystallizations from aqueous acetone melted at 190° and gave a purplish solution in acetone, benzene and chloroform. On warming an alcoholic solution of silver nitrate was reduced to the metal.

Found: I = 21.3%, 21.4%. Calculated for $(\text{OsI}_2 \cdot 3\text{Ph}_2\text{MeAs})_2$: I = 21.6%.

Di-Iodo-Hexakis-Dimethylphenylarsine-Diiodo-Osmium. When tris-dimethylphenylarsine tribromo osmium in aqueous acetone solution was refluxed with hydriodic acid a mixture of substances was obtained. The least soluble fraction after fractional crystallization from aqueous acetone gave purplish black needles, m.p. 175° . This substance was apparently the analogue of the compound described above. No trace of the green compound was noted, and the intermediate fractions gave analyses for iodine intermediate between a compound of osmium II and osmium III.

Found: I = 25.3%, 25.6%. Calculated for $(\text{OsI}_2 \cdot 3\text{PhMe}_2\text{As})_2$: I = 26.55%.

Hydrogen-Tri-n, Butyl-Phosphonium-Hexabromo-Osmate. Potassium hexabromo osmate (0.5 g.) was dissolved in hydrobromic acid (30 ml., 3 N.) and treated with tributyl phosphine (0.6 g., 3 mols.) in alcohol (30 ml.). The mixture was heated to 80° , when a red crystalline precipitate came down. The substance after recrystallization from alcohol melted at 171° . If the original preparative mixture was heated for more than a few minutes the red substance decomposed and the phosphine was oxidized to the phosphine oxide.

Found: Br = 44.1%. Calculated for $((\text{C}_4\text{H}_9)_3\text{H.P.})_2 \cdot \text{OsBr}_6$: Br = 44.47%.

Hydrogen-Tri-n, Butyl-Phosphonium-Hexachloro-Osmate. Prepared as the bromo compound above this gave a bright yellow crystalline powder, soluble in alcohol and acetone, m.p. 158° .

Found: Cl = 26.5%. Calculated for $((\text{C}_4\text{H}_9)_3\text{H.P.})_2 \cdot \text{OsCl}_6$: Cl = 26.4%.

SUMMARY.

Like ruthenium, osmium IV in the form of the hexahalogenates fails to yield complexes with tertiary arsines, which first reduce the element to the trivalent state, and then form simple unbridged, hexavalent complexes of the type $\text{OsX}_3 \cdot 3\text{AsR}_3$. Reduction of these compounds with hypophosphorous acid leads to the formation of osmium II complexes of the forms $\text{OsX}_2 \cdot 4\text{AsR}_3$ and $(\text{OsI}_2 \cdot 3\text{AsR}_3)_2$.

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THE COLORIMETRIC ESTIMATION OF STRYCHNINE.

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The importance of having available methods for the estimation of small quantities of potent alkaloids such as strychnine cannot be stressed too much. Owing to the small dosage of this substance, most methods for control in the manufacture of hypodermic injections and tablets require rather large amounts of material. Hypodermic tablets of strychnine are made in strengths varying from 1/20th to 1/100th grain, generally as sulphate, so that for the usual volumetric analysis from 20 to 100 tablets may be required. This number may be readily at hand during manufacture, but once distributed, a definite restriction appears in the amount available for assay. Also, the result thus obtained represents an average content, and for closer control in the mixing of medicament and base, the analysis of single tablets is useful. In these circumstances, colorimetric processes become of value.

Both reduction and oxidation procedures have been suggested for the determination of small amounts of strychnine. Malaquin (1909) introduced a characteristic reaction, which consisted of reduction by granulated zinc and hydrochloric acid, a rose red colour then being produced with sulphuric acid. Denigès (1911) modification of this test, reduction with zinc amalgam in a boiling water bath followed by treatment with sodium nitrite, was used by Allport and Jones (1942) for the examination of hypodermic tablets and by Allen and Allport (1940) for preparations of *nux vomica*.

Oxidation tests are more simply carried out and have been used for the identification of the alkaloid. Mandelin's reagent—solution of ammonium vanadate in sulphuric acid—has been suggested by Scandola (1911) for the estimation of small quantities. This reagent was tried during the present work but suffers from several disadvantages. When strychnine is treated with oxidizing agents such as ammonium vanadate, potassium dichromate, etc., in sulphuric acid, it passes through several colour changes. First, there is obtained a very intense purple colour which gradually fades and is replaced by more reddish shades, and the final colour is cherry red. Since this reagent itself is rather deeply coloured (reddish orange), the different colour changes during oxidation of small quantities may be masked to a large extent. Thus it is unsuitable for the technique employed in the present method. Garratt (1937) has suggested triturating small residues of strychnine with a large excess of solid ammonium vanadate and a few drops of sulphuric acid. Under these conditions it is difficult to ensure good contact and the procedure generally offers little advantage over the solution of the oxidizing material.

Cerium oxide is another oxidant commonly used. This occurs as brown material only slightly soluble in sulphuric acid, and although very useful for qualitative purposes, is generally unsuitable for quantitative work.

Ceric sulphate, however, is available as a clean, orange substance, readily soluble in water. It is not very soluble in sulphuric acid, but, on warming, sufficient dissolves to give a solution which is only faintly coloured, and which gives strong tests with small amounts of strychnine. By standardizing the

amount of reagent and the time allowed for the reaction, the use of this reagent for colorimetric estimations becomes possible. The reagent is very sensitive and a range of standard colours with a lower limit of 0.005 mg. strychnine may be used in the very simple procedure described below.

EXPERIMENTAL.

(a) Reagents.

- (i) *Solution of ceric sulphate in sulphuric acid.* Ceric sulphate, 1.0 g., powdered and warmed on steam bath for 20-30 minutes with sulphuric acid, 100 ml., stirring occasionally. Excess ceric sulphate is then removed by allowing to settle or by centrifuging. The finer particles settle rather slowly and even after centrifuging, the solution may be slightly turbid with suspended material. However, it may be used if not quite clear, provided, of course, the distribution of insoluble material is maintained during the estimation.
- (ii) *Strong solution of strychnine.* Strychnine 0.1 g., dissolved in chloroform 100 ml. (1 ml. \equiv 1 mg. strychnine).
- (iii) *Dilute solution of strychnine.* Prepared by diluting 1 volume of strong solution to 10 volumes with chloroform (1 ml. \equiv 0.1 mg. strychnine).

(b) Preparation of Standards.

Gently evaporate to dryness over a steam bath in small porcelain crucibles, about 15 ml. capacity, amounts of dilute solution of strychnine ranging from 0.1 to 1.0 ml. (0.01-0.1 mg.). To each residue, when cool, add solution of ceric sulphate, 2 ml. (Add the reagent to standards and unknown without stirring.) Briskly stir the contents of each crucible with a small glass rod for a few seconds at a time so as to develop the range of colours as far as possible at the same time. Compare unknown and standards after 2-3 minutes colour development for preliminary estimation. Allow to stand 10-15 minutes and make final comparison. Perform a blank experiment.

DISCUSSION OF METHOD.

(a) *Colour of Blank.* While there is a very slight yellow colour in the blank due to the reagent, the colour from as little as 0.005 mg. strychnine is easily distinguishable.

(b) *Colour Changes.* On stirring, the colour in each crucible soon becomes purple, with greater intensity in those containing the larger amounts of strychnine. The introduction of reddish tints then begins, and since these appear more rapidly with smaller amounts of strychnine, in the interval of 2-3 minutes after addition of the reagent, there is a range of colours from more or less reddish solutions with little purple to those still containing a considerable proportion of purple which are also more intense in colour. In all cases the purple colour disappears completely on further standing and finally there is a range of intensity in the same reddish orange colour. The reagent appears to deteriorate on keeping and ultimately loses its faint yellow colour. This leads to a variation in the rate of colour change so that the time periods given above may vary slightly according to the age of the reagent.

(c) *Colour Comparison.* As mentioned, use is made of the initial series of colours for an indication of the amount of alkaloid present. The strongest colour is at the purple stage, and the method would be even more sensitive if the reaction could be stopped at this point.

The final reddish orange colours are more readily compared at the lower end of the range, up to 0.5 ml. of dilute solution of strychnine, and it is suggested that for larger amounts a repeat experiment with a smaller aliquot be performed, also using fewer standards, so that the colours develop more evenly. The larger

amounts may possibly be more readily matched after diluting to 5 ml. with sulphuric acid and transferring to half-inch test tubes.

(d) *Determination of Amount of Material to be Used.* With a little practice it is not necessary to prepare a complete range of standards. It is possible to use the initial purple intensity to determine whether a smaller aliquot would be desirable to bring the final colour to the more sensitive portion of the range.

(e) *Stability of Colour.* The final colour fades on keeping, but the relative intensities are maintained for some time. A series of experiments was performed in which the coloured solution was diluted with water. Although a range of colour was obtained, it was not as permanent as when left in concentrated acid.

(f) *Stirring.* With the small amounts of strychnine present, efficient stirring is necessary to bring the film of alkaloid into contact with the reagent. The short periods of stirring should be continued at least until the reddish shades appear.

(g) *Interfering Materials.* Separation from the lactose of hypodermic tablets is necessary, as this affects the ceric sulphate.

The method is also subject to the usual interferences with oxidation tests for alkaloids.

(h) Porcelain crucibles provide a good background for the comparison of colours.

PROCEDURE FOR HYPODERMIC TABLETS.

Dissolve one tablet in distilled water, 5 ml., in a small separator, 25 ml. capacity. Add chloroform, 10 ml., make alkaline with dilute solution of ammonia, and shake vigorously during several minutes for extraction. Allow the layers to separate and filter the chloroform layer through a small plug of cotton wool, previously washed with chloroform, into a 25 ml. graduated flask. Continue the extraction with two further quantities of chloroform, 10 and 5 ml. respectively, passing these in turn through the filter. Finally, adjust the volume to 25 ml. with more chloroform. One ml. of this solution is evaporated and treated as described.

The range of standards above will just cover hypodermic tablets of strengths ranging from 1/20th to 1/100th grain of strychnine, as sulphate, using the dilutions suggested. For strengths above 1/40th grain it is preferable to reduce the amount of solution used to 0.5 ml.

EXAMINATION OF TABLETS.

Tablets of three strengths from one manufacturer were examined with the results summarized in the following table :

Labelled Strength as Strychnine Sulphate.	Equivalent in Strychnine Alkaloid.	Volume of Final Solution Used in Assay.	Equivalent of Dilute Solution of Strychnine.	Total Amount of Strychnine Found.
1/60th grain ..	0.84 mg.	1.0 ml.	0.30 ml.	0.75 mg.
1/40th " ..	1.26 mg.	1.0 ml.	0.45 ml.*	1.12 mg.
1/30th " ..	1.68 mg.	0.5 ml.	0.30 ml.	1.50 mg.

* This result obtained by interpolation.

SUMMARY.

A method is presented for the estimation of small quantities of strychnine, based on the colour produced by the action of ceric sulphate in sulphuric acid, and a procedure suggested for the examination of hypodermic tablets.

The method has been applied to the examination of hypodermic tablets.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD.

PART I. GEOLOGY OF THE WILLOW TREE DISTRICT.

By F. N. HANLON, B.Sc., Dip.Ed.
Geological Survey of New South Wales.

With Plate VII.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The North-Western Coalfield of New South Wales comprises an area extending from the Nandewar Mountains, north-east of Narrabri, to the vicinity of Blandford, a distance of approximately 150 miles.

The geological survey of the coalfield was included in the programme of the New South Wales Geological Survey. Field work commenced in 1945 and has been proceeding continuously during field seasons since that date. A considerable amount of field work still remains to be completed. The work has been concentrated on the study of the Permian rocks, formations of other ages being studied only in so far as was necessary to map the boundaries of the Permian system and elucidate the structural geology of the area.

It is proposed to publish the work in a series of papers, based on reports made to the New South Wales Department of Mines, dealing with different sections of the area. Although the bulk of the work carried out so far has been centred on the Gunnedah-Curlew district, the geology of the Willow Tree district is being published first because it provides the clue to the correlation of the Permian Sequence of the North-Western Coalfield with the type area in the Hunter Valley.

TOPOGRAPHY AND ACCESS.

Willow Tree is 1,390 feet A.S.L. and is situated in the County of Buckland on the New England Highway and the Great Northern Railway Line, being 233 miles by rail from Sydney. The area shown on the Geological Map of the Willow Tree district (Plate VII) extends about $2\frac{1}{2}$ miles in a north-westerly and south-easterly direction and is about one mile wide. Relief is moderate, the highest point surveyed being 570 feet above the level of the railway station or 1,960 feet A.S.L.

The central portion of the area is occupied by the valley of Borambil Creek, which has been eroded on the softer Permian rocks. The south-western edge is occupied by a line of hills composed of Triassic rocks capped in places by Tertiary basalt. Carboniferous rocks occupy a corresponding line of hills to the north-east.

The survey was carried out by means of a telescopic alidade and plane table. Contours at intervals of 50 feet are shown on the Geological Map of the Willow Tree district (Plate VII).

GEOLOGY.

The geological formations comprise the following :

Tertiary to Recent	Alluvium.
Tertiary	Basalt flows and dykes.
Triassic	Conglomerates and sandstones.
Permian—	

Borambil Series	Upper Stage	Soft claystones, sandstones, conglomerates and thin limestone bands.
	Lower Stage	Sandstones and conglomerates with Upper Marine fossils.
Willow Series	Upper Stage	Shales, sandstones, conglomerates and coal seam. <i>Glossopteris</i> present.
	Werrie Stage	Mainly amygdaloidal basalts.
	Lower Stage	Sandstones, shales, tuffs, conglomerates and carbonaceous beds. <i>Glossopteris</i> present.

Carboniferous—

Upper Kuttung	Upper Glacial Stage	Conglomerates, varves, tuffs.
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The rocks will now be described in detail, commencing with the oldest.

Carboniferous.

The only Carboniferous rocks mapped form a small outcrop in the north-eastern section of the area. They comprise the uppermost beds of the Upper Glacial Stage of the Upper Kuttung as described by Carey (1934, 1937) in connection with the geology of the Werrie basin. They consist of fluvio-glacial conglomerates, varves and a thin bed of tuffs which is probably the topmost bed of the Carboniferous system, although it could be the basal bed of the Permian. Micro-sections of the tuffs show excellent examples of shards.

Permian.

The discovery of Upper Marine fossils in sandstones outcropping along Borambil Creek has rendered necessary a complete reclassification of the Permian strata of the Willow Tree area. Owing to some uncertainty in the correlation with the Hunter Valley sequence and the unsuitability of the terminology for application to the Willow Tree strata, it is considered advisable to give the series local names, and the classification shown above is suggested. It is proposed to describe the sequence first and leave the discussion of the correlation until later.

Willow Series. This series consists of two groups of freshwater sediments separated by a considerable thickness of lava flows. It has been divided into three stages which are shown below, together with their probable thicknesses.

Upper Stage	..	More than 1,050 feet	} 3,450 feet
Werrie Stage	..	Less than 2,400 feet	
Lower Stage	..	300-550 feet	
Total thickness	..	4,000 feet	

The Lower Stage consists of sandstones, shales, tuffs, conglomerates and carbonaceous beds. They are continuous with rocks mapped by Carey (1934, 1935) in the Werrie Basin, from which he recorded the presence of the *Gangamopteris-Noeggerathiopsis* flora. He and Raggatt (1932) recorded the occurrence of coal seams in the beds at Currabubula and in the parishes of Quirindi, Coeypolly and Werrie, County of Buckland.

There is no sharp line of demarcation of the top of the Lower Stage, the uppermost strata being interbedded with flows of amygdaloidal basalt belonging to the Werrie Stage. This stage is the southerly continuation of the Werrie basalts mapped by Carey.

The boundary between the Werrie and Upper Stages of the Willow Series is entirely obscured by the alluvium along Borambil Creek. The section of the Upper Stage available for examination comprises about 900 feet of the topmost beds which outcrop along the south-western bank of Borambil Creek. A coal seam of good quality, probably at least 10 feet thick was struck in a well shown on Plate VII. The strata exposed consists of shales, sandstones, grits and conglomerates and contain bands of concretionary ironstone. Impressions of *Glossopteris* are plentiful.

Borambil Series. This series has been so named because of its occurrence along and to the west of Borambil Creek and has been divided into two stages.

The Lower Stage consists of sandstones and conglomerates and shows current bedding in places. On one horizon the following suite of fossils has been found :

Spirifer sp. indet.

Spirifer duodecimcostata McCoy.

Spirifer vespertilio Sowerby.

"*Martiniopsis subradiata*" Sowerby (large var.).

Merismopteria macroptera (Morris).

Deltopecten subquinelineatus Eth. and Dun.

Pelecypod (internal cast) indet.

The stage appears to be somewhat lenticular, the maximum thickness being 350 feet.

The Upper Stage is at least 2,000 feet thick and is composed of soft claystones, sandstones, conglomerates and thin beds of limestone. The latter are concretionary, at least in part, and may be equivalent to the calcareous concretions found at different horizons in the Mulbring Stage of the Upper Marine (Raggatt, 1929*b* ; Morrison and Raggatt, 1928). The rocks are soft, easily eroded and form poor outcrops. No fossils have been found in this stage and it is impossible to state definitely whether they are of marine or freshwater origin.

There is a small isolated outcrop of soft clayey and carbonaceous beds beneath the Triassic cliffs at the head of the main branch creek north of Oaklyn Homestead. They may be distinct from the Upper Stage of the Borambil Series, but have been included with them for mapping purposes.

Correlation.

Previous workers (Carey, 1934, 1935 ; Raggatt, 1938*a*) classified all the sediments overlying the Werrie basalts (Borambil Series and Upper Stage of the Willow Series) as Upper Coal Measures, the basalts themselves as Upper Marine and the underlying freshwater sediments as Lower or Greta Coal Measures, although Carey (1935) discussed the possibility that the last may correspond to an horizon in the Lower Marine Series.

The key to the correlation with the Permian Sequence of the Hunter Valley is provided by the marine fossils discovered in the Lower Stage of the Borambil Series. It is not possible to give an exact correlation of the fossiliferous horizon with the Upper Marine sequence of the type area. The lithology of the rocks would favour correlating them with either the Murree or Braxton Stages. However, Mr. H. O. Fletcher states : "The facies of the marine fossils indicates a geological age fairly high in the Upper Marine Series of the Permian." In the absence of fossil evidence on which to base an opinion, the correlation of the

Upper Stage of the Borambil Series must be doubtful, but it is considered that it is probably equivalent in part to the Mulbring Stage of the Upper Marine, and in part to the Tomago Stage of the Upper Coal Measures.

The outcrop of clayey and carbonaceous rocks referred to above may be an integral part of the Upper Stage of the Borambil Series or may represent part of the Newcastle Stage of the Upper Coal Measures, immediately underlying and conformable with the Triassic rocks.

The Upper Stage of the Willow Series is the equivalent, at least in part, of the Lower or Greta Coal Measures. However, because of the doubt as to the exact position of the fossiliferous horizon in the Upper Marine sequence and the possibility that some of the *Glossopteris*-bearing sediments may be a freshwater equivalent of portion of the Upper Marine of the Hunter Valley, it is considered preferable to refer to the sediments as the Upper Stage of the Willow Series. In the Cessnock district the Greta Seam forms the topmost bed of the Lower Coal Measures, which range in thickness from 100 to 300 feet (Jones, 1939). The roof of the coal seam at Muswellbrook is 75 feet from the top of the Lower Coal Measures and the total thickness of Greta sediments is 370 feet (Raggatt, 1929a). At Willow Tree, if we assume that there has been no normal strike faulting or igneous intrusives which are obscured by the alluvium along Borambil Creek, the coal seam is at least 1,050 feet from the top of the Upper Willow Stage and the total thickness of the stage probably greater than this figure. Any thrust faulting present would increase these estimates. The conditions could be explained by considering the top portion of the Upper Willow Stage as being a freshwater equivalent of part of the Upper Marine of the Hunter Valley or by an increase in thickness of the Greta sedimentation. In the latter alternative the Willow Tree coal seam may also be a separate seam developed at a much lower horizon than the Greta Seam.

David (1907) records from the Seven Mile near Raymond Terrace the occurrence of freshwater sediments, which contain abundant tuffaceous bands and a coal seam, and which underlie a thick formation of amygdaloidal basalts. He assigned them to the Lower Marine, and the writer considers that the Permian freshwater sediments and the overlying Werrie Basalts at Willow Tree are approximately on similar horizons. Browne and Dun (1924) also record the presence of a sandstone formation, tuffaceous in appearance, underlying amygdaloidal basalt near Lochinvar. The authors state that "The lower parts contain indeterminate plant stems and it was from the upper portions, which are in places pebbly, that the marine fossils were obtained". A similar relationship is found in the Loder's Mount area (to be described in Part II of the Geology of the North-Western Coalfield), where Lower Marine fossils have been found in the topmost beds of the stage. Amygdaloidal basalts which were probably contemporaneous with the above also occur in the Muswellbrook and Wingen-Murrurundi districts. The Lower Marine Basin probably occupied much the same area throughout the whole of the Lower Marine time, but the proportion of the basin which was open to the sea varied considerably. At times considerable areas would appear to have been occupied by freshwater lakes, although some of the plant-bearing horizons, particularly where the plant remains are fragmentary and could have been carried into the sea, may have been laid down under marine conditions. Basalt flows were poured into the basin throughout the whole of the area under consideration and the greater thickness of basalts in the Werrie Basin may be due to the continuation of volcanic activity in that area while sedimentation was proceeding in the Lower Hunter Valley.

Triassic.

Only the basal portion of the Triassic System was examined. It consists of coarse conglomerates which are interbedded with fine conglomerates and sandstones. It is characterised by the presence of abundant jasper pebbles and is similar to the basal portion of the Triassic as exposed throughout the North-Western Coalfield in sections already surveyed in detail.

Tertiary.

Tertiary basalt occurs as a capping to the line of hills along the south-western edge of the area mapped. It overlies the Triassic rocks and in places obscures completely the junction between the Triassic and Permian rocks. It also occurs as isolated outcrops and as dykes in the Permian rocks.

Tertiary to Recent.

The alluvium along Borambil Creek consists of black sticky clay containing gravel beds which yield good supplies of underground water at shallow depths. It has been derived mainly from the weathering of the Werrie and Tertiary basalts of the neighbourhood.

STRUCTURAL GEOLOGY.

The structural geology of the area is extremely interesting. For a full discussion it would be necessary to consider neighbouring areas, and the present discussion will be confined to the area mapped.

A cross-section of the area is shown in Plate VII. The portion beneath the Triassic rocks can be regarded as diagrammatic only.

Broadly speaking, the area surveyed may be regarded as being situated on the south-western limb of an anticline, whose axis trends in a north-westerly direction. The core of the anticline consists of Carboniferous rocks and the flank of Permian sediments. On the eroded edges of the latter the Triassic beds were laid down unconformably.

On the hill in the north-eastern corner of Plate VII the dips in the Carboniferous are low, being about 12°. Proceeding in a south-westerly direction the dips steepen until the Lower Stage of the Willow Series, which dips at about 55°, is reached. The dip continues to steepen until it reaches about 65°, and with few exceptions all outcrops between this point and the Triassic rocks dip at this angle or more steeply. Vertical dips are common and in places the beds are overturned; in one place a dip of 70° in the opposite direction was measured.

It was impossible to measure the dip of the clayey and carbonaceous beds at the head of the main branch creek north of Oaklyn Homestead. It is, therefore, impossible to state whether they dip in conformity with either the Borambil Series or the overlying Triassic rocks.

To what extent the sediments are affected by strike faulting in the section occupied by the Werrie Basalts and the alluvium along Borambil Creek it is impossible to say. It has certainly been affected by oblique faults which trend parallel to thrust faulting further to the north-east and are related to it.

An outcrop of finely bedded shaley sandstones occurs beneath the alluvium in the bed of the main creek north of Oaklyn Homestead and dips to the north-east at 35°. It is bounded on the south-west by a fault and on the north-east by creek alluvium. It probably represents portion of a block which has been caught between two faults, thus accounting for the anomalous dip.

The Triassic rocks have a general dip in a south-westerly direction which averages about 15°. They cross the line of the strike of the Borambil Series in the northern section of the area mapped and the isolated outcrop of Triassic

conglomerate in this section is surrounded on three sides, at least, by vertically dipping Permian strata. It is considered impossible to explain the relationship of the Triassic to the Borambil Series without postulating an almost right-angled unconformity between those formations.

It is considered that the folding of the Permian and Carboniferous at Willow Tree took place before the close of Upper Coal Measures time because the degree of unconformity existing between the Permian and the Triassic would require a period of erosion prior to the deposition of the latter. Also the outcrop of clayey and carbonaceous beds at the head of the main creek north of Oaklyn Homestead may be conformable with the Triassic rocks and represent portion of the Newcastle Stage.

In connection with the determination of the lower limit of the commencement of the folding, the first manifestation of the late Palæozoic diastrophism was recorded by David (1907), who observed the fact that the folding of the Lochinvar anticline commenced at the end of Muree time. However, at Willow Tree there is at least 2,000 feet of strata lying apparently conformably above what may be the equivalent of the Muree.

Raggatt (1938b) considered that Mulbring and Tomago time together represented a period of quiescence between the commencement of folding in Muree time and uplift of the surrounding land which he considered took place in Newcastle time. The writer has observed an interesting structure in a cutting on the Pelaw Main railway line at the point where it is crossed by the East Maitland-Mulbring Road. The Tomago Coal Measures west of the tunnel and in a small section near the base of the cutting east of the tunnel dip at about 35° - 40° , while the remainder of the sediments east of the tunnel dip at approximately 10° . The main portion of the junction between the two groups of sediments is obscured by the tunnel, but where visible dips at about 10° and is parallel to the bedding of the overlying sediments. The lowest bed of the more flatly dipping sediments contains small pebbles near its base and appearances favour regarding the relationship as an unconformity. If it is due to faulting it would be in the nature of a low angle overthrust which shows no signs of dragging the underlying sediments along the thrust plane in the section exposed. If the section represents a local unconformity situated not far below the accepted junction between the Tomago and Newcastle stages of the Upper Coal Measures, it would show that some folding of the Permian took place at that time and would furnish additional evidence on which to base an estimate of the age of the commencement of folding at Willow Tree.

It is considered that the folding probably commenced about the beginning of the Newcastle age. However, all the faulting did not take place in the pre-Triassic time because the Triassic and Lower Jurassic (Lower Comiala) in the vicinity of Murrurundi are dragged up against the Carboniferous, along a thrust fault, until they are dipping nearly vertically.

At Willow Tree there appears to have been minor normal faulting, probably during Tertiary time, along the margin of the Triassic rocks, which explains the outcrops of Triassic conglomerate below the general level of the main Triassic conglomerates further west. On Plate VII the fault has only been shown on the northern section of the map. It probably continues along Toll Bar Ridge east of the main mass of Triassic conglomerate and would explain the occurrence of abundant Triassic conglomerate pebbles on a number of hills below the level of the main outcrop and separated from it in many instances by a saddle. It was thought preferable not to show the fault continuing further to the south because its exact location is somewhat doubtful, and although Triassic conglomerate pebbles are very abundant on the hills, actual outcrops are wanting in most instances.

The unconformity between the Triassic and Permian is regarded as being only of local occurrence and marking approximately the position of the Triassic shoreline. It is considered that the dips in the Permian would quickly flatten in a south-westerly direction, the Newcastle stage of the Upper Coal Measures would progressively increase in thickness, and the Triassic and Permian would have their usual conformable relationship.

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I was assisted on the present survey by Mr. J. C. Lloyd, B.Sc., who was responsible for the instrumental work in connection with the alidade survey, and drafting of the plan to accompany this paper. Many helpful discussions with him on points raised during the progress of the survey are gratefully acknowledged. I am indebted to Mr. H. O. Fletcher, of the Australian Museum, for the determinations of the Upper Marine fossils. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

The Permian rocks of the Willow Tree area form the south-western flank of an anticline whose core consists of Carboniferous strata. The Permian probably comprises the equivalents of the Lower Marine sediments (represented by freshwater beds) and lavas, Lower Coal Measures, Upper Marine and Tomago Stage. They were probably folded prior to the deposition of the Newcastle Stage. The Triassic was laid down unconformably on the eroded edges of the Permian strata along the south-western boundary of the area. It is considered that the degree of unconformity would lessen markedly in a south-westerly direction and the relationship between the Triassic and Permian would become conformable.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD.
PART II. GEOLOGY OF THE WILLOW TREE-TEMI DISTRICT.

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With Plate VIII.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The Liverpool Range forms the southern and eastern boundary of the Willow Tree-Temi area. To the north of Willow Tree it adjoins the Werrie Basin mapped by Carey (1934, 1935, 1937). It includes the Willow Tree area, the geology of which was described in Part I of the Geology of the North-Western Coalfield (Hanlon, 1947).

The survey was in the nature of a close reconnaissance and the more detailed work has been confined mainly to the Permian system.

TOPOGRAPHY AND ACCESS.

The area is situated entirely within the south-eastern part of the County of Buckland and comprises the Parish of Temi, with portions of the Parishes of Loder, Quirindi and Warrah and the Warrah Estate. It is traversed by the New England Highway and the Main Northern Railway Line. Ardglen, adjacent to the Liverpool Range, is 226 miles by rail from Sydney, and Willow Tree is 233 miles. Access by roads to some sections are good, while others are accessible only by horse or on foot. Many roads shown on the parish maps either do not exist, or if ever constructed are now untrafficable.

Topographic relief is considerable. The lowest section of the district is adjacent to Willow Tree, which is less than 1,400 feet above sea level, while Mt. Temi, or Bother Jimmy as it is known locally, is approximately 4,113 feet A.S.L. The positions of creeks, particularly small tributary creeks, shown on the parish maps are inaccurate in most instances and on the geological map to accompany this paper (Plate VIII) the positions of many of them have been replotted. This has been done particularly in the portions of the Parishes of Temi and Loder, in which Permian strata outcrop.

Generally speaking, the more elevated sections of the area are occupied by Tertiary igneous rocks or Carboniferous strata, the lower lying sections consisting of the Permian beds.

GEOLOGY.

The classification adopted in Part I of the Geology of the North-Western Coalfield (Hanlon, 1947) is retained. It comprises the following formations which are described in detail below, commencing with the oldest.

Tertiary to Recent.

Tertiary.

Triassic.

Permian—

Borambil Series.

{ Upper Stage
Lower Stage

Willow Series.

{ Upper Stage
Werrie Stage
Lower Stage

Carboniferous—

Upper Kuttung Series.

Upper Glacial Stage

Carboniferous.

The survey was not directly concerned with the Carboniferous stratigraphy and it was not studied in any great detail except in the northern part of the area mapped, where it was necessary in order to trace the positions of some of the faults shown.

The strata belong to the Upper Glacial Stage of the Upper Kuttung as described by Carey (1934, 1937) in connection with the geology of the Werrie Basin. They consist of fluvio-glacial conglomerates, varves, tuffs and acid lavas. The varves in places show very sudden lateral variation into conglomerates, the change being so sudden at times as to resemble a faulted junction.

Where developed, acid lavas or tuffs seem to form the top of the Carboniferous system. However, these beds are lenticular and in many places the Permian strata are resting directly on either conglomerates or varves.

Permian.

The conclusions reached previously (Hanlon, 1947) as to the age of the various stages of the Permian strata might be stated briefly here. The Lower Stage of the Borambil Series consists of sandstones and conglomerates with Upper Marine fossils. The Upper Stage comprises soft claystones, sandstones and conglomerates with thin limestone bands, and is unfossiliferous. It is probably equivalent in part to the Mulbring stage of the Upper Marine and in part to the lower portion of the Upper Coal Measures. The Borambil Series is found only at Willow Tree. It has been described previously (Hanlon, 1947) and the description will not be repeated here. The Willow Series is considered to be equivalent to both the Lower Coal Measures and the Lower Marine Series of the Hunter Valley. It will be described now.

Willow Series.

The Upper Stage consists of shales, sandstones, grits and conglomerates and contains bands of concretionary ironstone, as well as a seam of good quality coal, at least 10 feet thick. Details of the occurrence of the coal seam have been given by Raggatt (1938). This stage only outcrops in the Willow Tree area and its correlation with the type area has already been dealt with (Hanlon, 1947). It was considered to be equivalent, at least in part, if not entirely, to the Greta or Lower Coal Measures.

It is underlain by the Werrie Stage, which consists mainly of amygdaloidal basalts. The lower portion is interbedded with sediments of the Lower Stage

of the Willow Series. The latter consists of sandstones, shales, tuffs, conglomerates and carbonaceous beds and is continuous with rocks mapped by Carey (1934, 1935) in the Werrie Basin, from which he recorded the presence of the *Gangamopteris-Noeggerathiopsis* flora. Although the beds contain plentiful plant remains, the only identifiable fragments consist of *Glossopteris*. The oil-shale, known as the Temi or Doughboy Hollow deposit, occurs within this stage. It has been described in some detail by David (1892) and Carne (1903). Both Raggatt (1932) and Carey (1935) record the presence of coal seams in the beds at Currabubula and in the Parishes of Quirindi, Coeypolly and Werrie, County of Buckland.

There is a local development of sediments composed of sandstones, grits, conglomerates, tuffs and agglomerates in the Temi Basin. In the vicinity of Loder's Mount there are three main groups, which are separated by flows of Werrie Basalts. Further south at the Devil's Pinch near Mt. Temi, the intervening basalts have largely lensed out. Rather than draw a boundary at the base of the lowest basalt flow and include the sedimentary bands in the Werrie Stage, or include some of the basalt flows in the Lower Stage by drawing the boundary at the top of the highest sedimentary band, it was thought preferable to map the individual sedimentary beds as belonging to Lower Stage and the lava flows as belonging to the Werrie Stage in order to delineate the structure more clearly.

Intrusive and extrusive masses of Tertiary basalt in the vicinity of Mount Temi and Jack White's Mountain have rendered accurate mapping of the Lower and Werrie Stages of the Willow Series in that locality very difficult. The area shown as Tertiary basalt between the basal substage and the beds outcropping at the Devil's Pinch probably consists of Werrie Basalts in part, but in the time available for the survey it was impossible to make any separation.

An interesting suite of marine fossils was collected from the topmost bands of Lower Willow sediments on the slopes of Loder's Mountain. The fossils were kindly identified for me by Mr. H. O. Fletcher, of the Australian Museum, who favours assigning them to about the middle of the Lower Marine Series. The list of fossils determined is as follows:

Spirifer sp. indet.

Spirifer cf. *stokesi* Konig.

"*Martiniopsis subradiata*" Sowerby (small var.).

Stutchburia farleyensis Etheridge.

Eurydesma cordata Morris.

Aviculopecten mitchelli Eth. and Dun.

Platyschisma ocula Sowerby.

Taking all the evidence into consideration it seems impossible to escape the conclusion that both the Werrie basalts and the interbedded and underlying sediments are equivalent in age to the Lower Marine Series of the Hunter Valley.

Triassic.

Only the basal portion of the Triassic system was examined. Three isolated outcrops occur and one of these in the north-west of the area has already been described (Hanlon, 1947). The other main outcrop is situated on a low hill between Borambil and Chilcott's creeks. A small outcrop, surrounded entirely by Tertiary basalt, occurs near the western boundary of the Parish of Temi, adjacent to the point where the Parish of Gregson adjoins the Warrah Estate.

The rocks examined consist of coarse conglomerates which are interbedded with fine conglomerates and sandstones. The coarse conglomerate is characterised by the presence of abundant jasper pebbles.

Tertiary.

Tertiary basalt and dolerite occupies quite a large proportion of the area mapped and occurs in the form of sills, dykes, flows and irregular intrusive masses. Two main centres of the igneous activity are located at Mt. Temi and Jack White's Mountain. Sills have been intruded in places between the Carboniferous and Permian rocks and at various levels in the basal portion of the Permian system.

Tertiary basalt occurs both above and below the basal portion of the Lower Willow Stage, which contains the oil-shale horizon adjacent to Mt. Temi. In the creek below the oil-shale mine, the Tertiary basalts can be seen intruding the Permian sediments. The basalts between the oil-shale horizon and the sediments at the Devil's Pinch probably consist of a sill or series of sills of Tertiary basalt intruded between the Werrie Basalts. In the time available during the course of the survey it was impossible to make any separation of the different basalts.

Flows of Tertiary basalt occur along the top and slopes of the Liverpool Ranges. The boundaries have not been traversed in detail and in many places are sketched. Isolated outcrops are found on the tops of many hills and along and adjacent to faults throughout the area.

Tertiary to Recent.

These deposits comprise the alluvium along Borambil and Chilcott's creeks. It consists of black sticky clay containing gravel beds and has been derived mainly from the weathering of the Werrie and Tertiary basalts. The gravel beds yield good supplies of underground water at shallow depths.

STRUCTURAL GEOLOGY.

The central portion of the area is made up of the Back Creek Dome and the elongated nose which forms the southern extension of the Castle Mount Dome. The latter is offset about two miles westerly from the northern nose of the Back Creek Dome. Together they form an anticlinal zone which trends west of north and has a core of Carboniferous rocks. The south-western limit of this zone is formed by Permian strata which are in turn overlain unconformably by the Triassic system (Hanlon, 1947). To the east lies the Temi Basin, so named because of its situation relative to Mt. Temi and the parish of the same name. It continues under the Liverpool Range and can be traced southwards until cut off by the Murrurundi thrust. Except for Tertiary basalt, the rocks outcropping in the basin belong entirely to the Lower and Werrie Stages of the Willow Series.

Several faults are shown on the Geological Map of the Willow Tree-Temi District (Plate VIII), and most of them are considered to be thrusts. Once the faults pass into the Werrie Basalts it is almost impossible to trace them for any great distance. The faulting may consist of a zone made up of a series of oblique thrusts arranged *en echelon*, in which case the faults in the north-west of the Temi Basin may die out southwards. If any of them continue they would probably pass immediately north of Jack White's Mountain, cross the Liverpool Range in the vicinity of Mt. Temi, and then continue through the Parish of Temi, County of Brisbane, north of the area to be described in Part III of the Geology of the North-Western Coalfield.

Where the area mapped joins the Werrie Basin the conclusions reached as to the structure differ somewhat from Carey's (1934) original interpretation. The Castle Mountain Dome is a fairly broad structure until its southern termination is reached. Here it narrows suddenly and its southern continuation is represented only by the relatively narrow nose referred to earlier. It is considered that the relief of the stresses developed during the folding was brought about by the formation of a series of thrusts, in some of which the movement was largely

horizontal, and that the present disposition of the strata can be explained in this way rather than by a series of later normal faults. (The Colly Creek faults of Carey.)

It is also considered that the Triassic shore line was not very far from the edge of the present Carboniferous hills along the Willow Tree-Quirindi Road, and that it is difficult to say to what extent the sudden change from the Carboniferous hills to the alluvial flats is due to faulting, and to what extent it is the result of shore line conditions, although it must have been caused partly by faulting.

The folding of the sediments and the thrust faulting are considered to be intimately related. The age of the folding has already been discussed (Hanlon, 1947). It only remains to add here that the local development in the Temi Basin of the higher bands of sediments belonging to the Lower Willow Stage shows that a synclinal structure commenced forming in the area as early as Lower Marine time. This development probably had considerable influence on the location of the Temi Basin during the main folding and faulting which took place in Late Permian time.

In the area between Mount Temi and Jack White's Mountain several faults were developed and would appear to be related to the intrusion of the igneous rocks during Tertiary time. Further movement along some of the thrust faults may also have taken place during the Tertiary period.

ACKNOWLEDGEMENTS.

I was assisted on the survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him are gratefully acknowledged. I am indebted to Mr. H. O. Fletcher, of the Australian Museum, for the determinations of the Lower Marine fossils. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

The area consists of Carboniferous, Permian and Triassic rocks which have been affected by intrusions and flows of Tertiary age. The Carboniferous forms the core of an anticlinal zone and the north-eastern flank of the Temi Basin, which is occupied by sediments and volcanics of Lower Marine age. The south-western flank of the anticlinal zone is occupied by Permian strata, which dip vertically in places and are overlain with an almost right-angled unconformity by the Triassic. It is considered that the degree of unconformity would lessen markedly in a south-westerly direction and the relationship between the Triassic and Permian would become conformable.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD.
PART III. GEOLOGY OF THE MURRURUNDI-TEMI DISTRICT.

By F. N. HANLON, B.Sc., Dip.Ed.
Geological Survey of New South Wales.

With Plate IX.

(Presented by permission of the Under Secretary for Mines.)

Manuscript received, November 19, 1947. Read December 3, 1947.

INTRODUCTION.

The area mapped adjoins the Willow Tree-Temi district (Hanlon, 1947*b*) along the Liverpool Range, and on the south the area mapped by Dr. H. G. Raggatt in the vicinity of Blandford and Wingen. The geology is shown on Plate IX. The boundaries on the eastern portion of the Parish of Murulla, County of Brisbane, between the Page's River and the railway line have been taken from unpublished maps by Dr. H. G. Raggatt.

The survey was in the nature of a reconnaissance and rocks not belonging to the Permian System were mapped only in so far as was necessary to determine the boundaries of the Permian, and the general structure of the area.

TOPOGRAPHY AND ACCESS.

The area is located in the County of Brisbane immediately south and east of the Liverpool Range and comprises parts of the Parishes of Isis, Murrurundi, Murulla, Temi and Timor. It is traversed by the New England Highway and the Main Northern Railway Line. Murrurundi is 219 miles and Blandford 215 miles from Sydney by rail. Access by road varies, although it is mostly fair. Some of the more mountainous sections are accessible only by horse or on foot.

Topographic relief is considerable. The lowest lying section of the district is adjacent to Blandford, which is less than 1,400 feet A.S.L., while the highest point is Mt. Temi, approximately 4,113 feet A.S.L. The positions of creeks, particularly small tributary creeks, shown on the parish maps are often inaccurate, and on the geological map to accompany this paper (Plate IX) the positions of some of them have been replotted.

Generally speaking the more elevated sections of the area are occupied by Tertiary igneous rocks or Carboniferous strata, the lower lying sections consisting of Permian beds.

GEOLOGY.

The rocks of the area comprise the following formations, which are described in detail below, commencing with the oldest :

Tertiary to Recent

Tertiary

Jurassic.

Triassic.

Permian

Upper Coal Measures

Upper Marine Series

Lower Coal Measures

Willow Series

{ Werrie Stage
Lower Stage

Carboniferous—

Upper Kuttung Series

Upper Glacial Stage.

Carboniferous.

The Carboniferous stratigraphy was not studied in any great detail. The strata belong to the Upper Glacial Stage of the Upper Kuttung and consist of fluvio-glacial conglomerates, varves, tuffs and acid lavas. The sudden lateral variation of the varves to conglomerates mentioned previously (Hanlon, 1947b) is shown very well along the lower part of Warland's Creek, where there are also excellent examples of contorted varves.

Permian.

The Murrurundi-Temi area forms a connecting link between the Permian strata of the Willow Tree district and the Upper Hunter. The Upper Coal Measures, Upper Marine Series and Lower Coal Measures are connected with beds of the same age, which have been mapped continuously from the south and the classification adopted in the type area has been retained for them. The Werrie and Lower Stages of the Willow Series are only partly connected by mapping with the Lower Marine of the Hunter Valley and the classification adopted in the Willow Tree area (Hanlon, 1947a) has been applied to them.

Willow Series. The Lower and Werrie Stages of the Willow Series are considered to be the equivalents of the Lower Marine of the type area in the Hunter Valley. However, only freshwater and no marine fossils were found in either stage in the Murrurundi-Temi district. The correlation has been discussed in detail previously (Hanlon, 1947a, 1947b). Although the strata below the Lower Coal Measures to the south of the area mapped have not been examined, descriptions of them suggest that a proportion of the uppermost beds which have been mapped as Carboniferous may belong to the Werrie and Lower Stages of the Willow Series.

Lower Stage. It consists of freshwater sediments comprising sandstones, shales, tuffs and carbonaceous beds and contains fragmentary plant remains. Mr. C. J. Ivin has collected *Gangamopteris cyclopteroides* from the Temporary Common in the Parish of Murulla and *Phyllothea australis* from the vicinity of portion 74, Parish of Temi. The formations mapped represent the basal sub-stage of the Willow Tree-Temi area (Hanlon, 1947b). Beds of tuffs, agglomerates and conglomerates are found interbedded with the Werrie Stage and would correspond to similar bands found on the northern side of the Liverpool Range. Time did not permit the individual boundaries to be traversed, and these bands have not been shown on the Geological Map of Murrurundi-Temi (Plate IX).

Sandstones which contain bands of oil-shale occur in the Parish of Temi to the north of the area mapped. They are considered to represent part of the Lower Willow Stage, which has been brought into its present position by faulting. The faulting is probably in part at least of Tertiary age and associated with the intrusion of Tertiary basalts and trachytes. Late Permian thrust faulting may also have affected the area.

Werrie Stage. It consists mainly of amygdaloidal basalts which weather rapidly and are always more or less decomposed. The lowest flows are interbedded with the upper beds of the Lower Willow Stage. In some places basalts similar to the typical Werrie Basalts occur below the base of the Lower Stage, between it and the Carboniferous. However, it is impossible to say whether they represent early flows or locally developed sills. They may even be Tertiary basalt sills.

Lower Coal Measures. They comprise shales, sandstones, grits and conglomerates with bands of concretionary ironstone and a coal seam. The nature of the sedimentation is essentially similar to that of the Upper Willow Stage of the Willow Tree district, although the total thickness of the sediments seems to be less than the probable thickness at Willow Tree, and the coal seam appears to be closer to the top of the series. The seam has been prospected adjacent to the Page's River on portion 65, Parish of Murulla, by means of an inclined shaft. South of the area mapped and north-east of Wingen township, the seam has been on fire for many years in the vicinity of Burning Mountain (David, 1907).

Upper Marine Series. It consists of conglomerates, sandstones and shales and has been mapped by Dr. H. G. Raggatt (unpublished) northwards from Wingen to the Page's River in the Parish of Murulla, where certain horizons contain an abundant marine fauna. The sediments continue across the Page's River and can be traced around the Sandy Creek syncline in the Parish of Isis. Near the boundary between the Parishes of Isis and Timor, a band of conglomerate near the base of the Upper Marine is overlain by shales containing abundant *Glossopteris* and plant remains and the resistant sandstone bands which are developed on the western limb of the syncline appear to be absent. It seems, therefore, that either the Upper Marine thins rapidly in this direction or else that marine give way to fresh water conditions. Northwards from Splitter's Creek the Upper Marine is not recognizable although adjacent to the Murrurundi Thrust there is a bed of conglomerate which may be the same as the conglomerate bed referred to above. However, in the absence of fossil evidence it is thought preferable not to map any Upper Marine but to show the Lower Coal Measures as grading out into the Upper Coal Measures.

Upper Coal Measures. The formations comprise conglomerates, in places very coarse, sandstones, shales and coal seams. The beds are mostly soft and easily eroded. In many places the beds closely resemble portions of the Upper Stage of the Borambil Series at Willow Tree. At some points the matrix of the conglomerates has weathered away to such an extent that the outcrops consist almost entirely of loose pebbles. Dr. H. G. Raggatt (unpublished) reported marine fossils above what was taken as the base of the measures.

Coal has been reported in many localities throughout the area, but the seams are mostly only one foot to 18 inches thick. The only exception is a thick seam which was struck in a well in portion 58, Parish of Murulla. It is probably dipping very steeply and is adjacent to the Murrurundi Thrust. The associated strata may represent a block of Lower Coal Measures which has been dragged up adjacent to the fault. However, in the absence of proof of a second fault in front of the Murrurundi Thrust, or the discovery of Upper Marine strata so

located as to explain the occurrence of Lower Coal Measures in this position, it is impossible to map the seam as belonging to any but the Upper Coal Measures.

Dips in the Upper Coal Measures vary from very steep to low. The upper beds are generally obscured by talus from the overlying Triassic conglomerates.

Triassic.

They consist of two stages, a lower conglomeratic stage and an upper sandy stage. The Lower Stage consists of conglomerates and sandstones and is characterized by abundant jasper pebbles in the conglomerates. Outcrops of bands of these conglomerates tend to form cliffs and make conspicuous physiographic features. The Upper Stage consists mainly of sandstones and shales, the latter being very lenticular. Good sections can be seen along the New England Highway between Murrurundi and the "Gap".

Jurassic.

A small outcrop of Jurassic shales occurs adjacent to the Great Northern Railway line to the south of the tunnel near Murrurundi Gap. Jurassic plants were discovered in these beds by Dulhunty (1939). They are very soft and form poor outcrops.

Tertiary.

Tertiary dolerites and basalts form widespread outcrops throughout the area mapped. They occur as flows, sills and dykes. Except for one small break at the Murrurundi Gap, the basalt is continuous along the crest of the Liverpool Range. Several isolated hills are capped by basalt.

At least one plug of trachytic composition occurs adjacent to the area mapped. Some of the outcrops of similar material within the Murrurundi-Temi district probably represent sills or dykes of Tertiary age. They occur within both the Carboniferous and Permian strata, but have not been mapped separately.

Tertiary to Recent.

These deposits are confined to the alluvium along the Page's River and its tributaries. The alluvium is derived from the coal measures and Carboniferous sediments as well as basalts. It is much lighter in colour and less clayey than that along Borambil Creek, north of the Liverpool Range, which is derived largely from the weathering of Werrie and Tertiary basalts.

STRUCTURAL GEOLOGY.

The area is divided into two portions by the Murrurundi Thrust. North of the thrust the structures represent the southerly continuation of the Back Creek Dome and Temi Basin which were obscured by Tertiary basalt along the top of the Liverpool Range. The formations exposed are similar, the core of the Back Creek Dome being composed entirely of Carboniferous rocks and the outcrops in the Temi Basin being confined to the Werrie and Lower Stages of the Willow Series, except for intrusions and flows of Tertiary age.

South of the Murrurundi Thrust the synclinal zone, of which the Temi Basin forms a part, is continued. It has been named the Sandy Creek Syncline from its relationship to the course of Sandy Creek. It is closed to the south, at least as low stratigraphically as the upper beds of the Werrie Stage, and the nose may have been affected slightly by faulting. The syncline pitches to the west of north and is flanked on the south-west by an anticline which pitches in conformity with it. The strata exposed are much higher stratigraphically than

those outcropping north of the Murrurundi Thrust and comprise portions of the Upper Coal Measures, Upper Marine Series, Lower Coal Measures and Werrie Stage, below which the mapping was not continued.

The relationship of the Triassic to the Permian is obscured by talus. However, although the Upper Coal Measures adjacent to the railway line dip steeply, there is no definite evidence of any unconformity between the two formations.

Numerous small faults occur in the area, particularly adjacent to the Murrurundi Thrust, but they have not been mapped because in most instances they are impossible to trace and can only be recognized at one point.

By far the most important fault in the area is the Murrurundi Thrust. It has a general east-west strike and has been traced from west of the Murrurundi Gap to the eastern edge of the area mapped and continues eastwards some distance beyond this point. It cannot be traced westwards because it passes beneath the Tertiary basalt. The isolated bar of steeply dipping Triassic sandstone in portion 63, Parish of Temi, referred to above, is almost on the continuation of the line of the fault. The northern side of the fault has moved upwards and westwards relative to the southern side. The amount of movement must have been considerable, because in the area immediately east of the Murrurundi Gap the Carboniferous strata is faulted so as to be above both the Triassic and Jurassic, which are dipping very steeply. This represents the complete elimination of the whole of the Permian system. If the thickness of the Permian here is comparable with that exposed at Willow Tree, it represents the elimination of well over 6,000 feet of strata without counting the thickness of Triassic and any Carboniferous beds which may be concealed. It is considered to be a thrust rather than a normal fault for the following reasons. Firstly, there is a northerly dipping fault zone on or adjacent to the line of the Murrurundi fault in portion 1b, Parish of Murrurundi. Secondly, there is a series of small thrust faults in the upthrown block adjacent to the main fault above Scott's Creek. From their relationship to the main fault they would be in the nature of underthrusts. Thirdly, the beds on the downthrow side of the fault have been dragged up until they are practically vertical. This applies without exception to the Jurassic, Triassic and Permian strata, and is considered to be more consistent with thrust than normal faulting.

The age of the folding and faulting have been discussed previously (Hanlon, 1947a, 1947b). The discussion will not be repeated except to draw attention to the outcrops of Triassic and Jurassic strata near Murrurundi Gap which have been dragged up along the fault until almost vertical and prove that at least some of the movement along it took place in post-Jurassic time.

ACKNOWLEDGEMENTS.

I was assisted on this survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. A. B. Walkom for the determination of the fossil plants collected by Mr. C. J. Ivin. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

I also wish to express my sincere thanks to Mr. C. J. Ivin, of Murrurundi, for information made available. Mr. Ivin is an amateur geologist who has made the geology of the Murrurundi district his hobby over a period of many years. His views coincide with the writer's in most instances. He recognized the synclinal areas which have been named by the writer, the Temi Basin and the Sandy Creek Syncline, and also traced the Murrurundi fault. He maintained the Werrie Basalts were of Lower Marine age, a contention which the writer has since proved correct. He also correlated the underlying freshwater sediments

on the opposite sides of the Liverpool Range, but differed from the writer's views by placing them in the Carboniferous. The main point of difference between his and the writer's views was that he considered the Temi oil-shale deposit and similar deposits on the Murrurundi side of the Liverpool Range as being Tertiary. He has also carried out a considerable amount of work on the Carboniferous and Devonian strata east of the area under consideration. His work has not been published and the writer considered that some mention of it should be made.

SUMMARY.

The area is divided into two portions by an east-west thrust fault and comprises a synclinal zone trending west of north which is flanked on the west by an anticlinal zone. Outcrops consist of Carboniferous, Permian, Triassic and Jurassic strata, together with intrusions and flows of Tertiary igneous rocks. The main folding and faulting was probably late Permian in age, but further considerable movement took place along the thrust fault at least as late as Jurassic and possibly during Tertiary time.

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Obituary.

FREDERICK STAPLETON MANCE was born in Parramatta in 1872 and died in Sydney on August 24th, 1945. He was educated at Sydney High School and entered the Public Service (Department of Mines) in 1890. After a distinguished career he was appointed Under-Secretary for Mines in 1928. Mr. Mance took a very great interest in all public activities and was closely associated with any movement that had as its objective the education and enlightenment of the public, especially the younger people. He was President of the Board of Trustees of the Australian Museum and belonged to our Society for twenty-one years. He is survived by a wife, son and daughter.

RICHARD OLD, a life member, died at his home on July 24th, 1945. He had been a member of the Royal Society for forty-three years.

JOHN POWELL, who was born in London eighty-one years ago, died in Sydney on July 24th, 1945. His early life was spent in Kent at his father's country store. After a few months at sea he became connected with the grocery trade in Maidstone, Kent. Following a successful business career, he joined the staff of Messrs. Foster, Clark Limited. In 1917 the firm sent him to Australia to commence manufacture here. He was made Managing Director of Foster, Clark (Australia) Ltd., and a director of Messrs. Peek Frean (Aust.) Pty. Ltd.

He attended London University and worked in History and Economics. He was a pioneer of adult education in England and brought to this country many ideas of the London School of Economics. He was a Fellow of the Royal Economic Society of London.

ALLAN CLUNIES ROSS died in Sydney on February 10th, 1946, at the age of 57. He was born at Bathurst, N.S.W., and was educated at All Saints' College, Bathurst, Sydney High School and the University of Sydney, where he graduated in Science in 1910. After graduation he taught physics and mathematics at the Townsville Grammar School and the North Sydney Church of England Grammar School.

He served as a sergeant in the 17th battalion, A.I.F., in the 1914-18 war, was gassed in France, was subsequently commissioned and served in the Army Education Service in England until the middle of 1919. During this war Mr. Clunies Ross served in the Commonwealth Directorate of Man-Power, first as Assistant Director of Scientific Personnel and then, up to his death, as Controller of Scientific Personnel.

On returning to Australia from World War I he qualified as an accountant and became an authority on finance, taxation and business administration, being elected President of the Commonwealth Institute of Accountants. Mr. Clunies Ross retained his early interest in education and was for a number of years Lecturer in Business Principles and Practice in the Faculty of Economics, University of Sydney, and in advanced courses in Business Administration under the University Appointments Board. The width of his interests and activities was evidenced by his membership of the Economic Society of Australia and New Zealand and of the Royal Society of New South Wales, in both of which he served for a number of years as a member of Council and as an Honorary Treasurer; he was also a foundation member and councillor of the Industrial Management. In addition, he was the author of several books on business and accountancy matters.

Mr. Clunies Ross had been the Honorary Treasurer of our Society since 1941, and his high ideals and his devotion to duty, as well as his professional skill, were recognized by all of us who had the good fortune to come in contact with him.

THOMAS HODGE SMITH died in Sydney on June 8th, 1945, at the age of 51. He was born at Swindon, Wiltshire, England, and was brought to Australia at the early age of two. He was educated at Scots College, Sydney Technical High School, Sydney Technical College, and the University of Sydney. He served with distinction in the Royal Australian Navy in New Guinea during 1914 and 1915, and from 1916 to 1918 in France, where he was severely wounded. After his return to Australia he again took up his position with the Department of Mines as a Geological Cadet, and subsequently became Assistant to the Mineralogist. In 1921 he joined the staff of the Australian Museum as Mineralogist, and in 1941, became Officer-in-charge of Preparation, Australian Museum.

In the scientific world Thomas Hodge Smith will be remembered as a morphological crystallographer and as an authority on Australian meteorites. In his early years as mineralogist at the Museum, he carried out a good deal of field work, especially as regards the occurrence of zeolite minerals in New South Wales and on the mica fields of central Australia. From 1925 until the time of his death he was teacher of mineralogy at the Sydney Technical College.

His scientific interests, apart from his official duties, were numerous. He was a Fellow of the Australian and New Zealand Association for the Advancement of Science, and an active member of a number of other scientific societies, including the Royal Society of New South Wales which he joined in 1922. In recent years he was the Chairman of the Section of Geology.

EDWARD SUTHERLAND STOKES, who was born at Newcastle, N.S.W., died at the age of 76 on April 12th, 1945. He was educated at the Newcastle Grammar School and subsequently studied medicine at the University of Sydney. His medical career was most varied, and he became an outstanding authority in problems of public health, particularly on the chemistry and bacteriology of water and the treatment of sewage. During the first world war he served as a member of the Australian Medical Corps, going abroad in 1914, and after return from Gallipoli, in 1915, he was promoted to the rank of Colonel and appointed to the position of Principal Medical Officer of the Second Military District. In 1917 he returned to the Water and Sewerage Board, where he had been Medical Officer since 1904.

After his retirement from the Board in 1935 he practised privately as a water technologist until 1942, when, due to the exigencies of the war, he returned to his old post, from which he finally retired in December, 1943.

LESLIE VICKERY WATERHOUSE was born in Sydney in 1886 and died on November 27th, 1945. He was educated at the Sydney Grammar School and the University of Sydney, graduating B.E. in Mining and Metallurgy in 1910. His undergraduate course was interrupted by a twelve months travel abroad. He joined the Broken Hill Proprietary Company in 1910 as an assistant assayer, where he made special investigations into the newly introduced flotation process and its particular applicability to the treatment of low grade copper ores. In associating himself with various mining concerns, he soon became established as a very successful mining engineer and made his influence felt. For many years he took a prominent place in the Australasian Institute of Mining and Metallurgy, acting as one of the New South Wales representatives on the Council, and becoming President in 1938. He played a very prominent part in the development of gold mining in New Guinea, and as a director of Guinea Airways did important work in developing air transport of heavy machinery and merchandise. He was a member of the Royal Society of New South Wales for twenty-three years.

PROFESSOR JAMES THOMAS WILSON died at Cambridge at the great age of 84 on September 2nd, 1945. During his stay in Sydney, from 1887 to 1920, he played an outstanding role in the community as an educator and organizer, and was one of the founders of the medical school of the University of Sydney. At the early age of 29 he was appointed to the newly created Challis Chair of Anatomy, a position which he occupied till he was invited to the Professorship of Anatomy in the University of Cambridge. In recognition of his outstanding contributions in the realm of Anatomy, he was made an Honorary Member of our Society in 1922.

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

April 2nd, 1947.

The Annual Meeting, being the six hundred and thirty-ninth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The President, Dr. F. Lions, was in the chair. Forty-three members and visitors were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

J. A. DULHUNTY, D.Sc.

Vice-Presidents :

R. L. ASTON, B.Sc., B.E. (*Syd.*), M.Sc.,
Ph.D. (*Camb.*), A.M.I.E. (*Aust.*).
F. LIONS, B.Sc., Ph.D., A.R.I.C.

H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

Hon. Secretaries :

D. P. MELLOR, D.Sc., F.A.C.I.

F. R. MORRISON, A.A.C.I., F.C.S.

Hon. Treasurer :

G. D. OSBORNE, D.Sc. (*Syd.*), Ph.D. (*Camb.*).

Members of Council :

R. C. L. BOSWORTH, M.Sc., D.Sc. (*Adel.*),
Ph.D. (*Camb.*), F.A.C.I., F.Inst.P.
R. O. CHALMERS, A.S.T.C.
H. O. FLETCHER.
F. N. HANLON, B.Sc.
W. H. MAZE, M.Sc.

R. S. NYHOLM, M.Sc.
D. J. K. O'CONNELL, S.J., M.Sc., F.R.A.S.
P. M. ROUNTREE, M.Sc. (*Melb.*),
Dip.Bact. (*Lond.*).
J. L. STILL, B.Sc., Ph.D.
O. U. VONWILLER, B.Sc., F.Inst.P.

The Annual Balance Sheet and Revenue Account were submitted to members. In the absence of the Honorary Treasurer, they were presented by Dr. D. P. Mellor, who moved the adoption. The motion was seconded by Dr. J. A. Dulhunty, and carried unanimously.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1947.

LIABILITIES.

1946.			1947.		
£			£	s.	d.
246	Accrued Expenses			92	3 2
13	Subscriptions Paid in Advance			14	14 0
68	Life Members' Subscriptions—Amount carried forward			60	0 0
	Trust and Research Funds (detailed below)—				
1,875	Clarke Memorial	1,908	13	8	
1,030	Walter Burfitt Prize	1,065	7	10	
726	Liversidge Bequest	700	0	0	
3,248	Research	3,322	8	4	
				6,996	9 10
25,775	ACCUMULATED FUNDS			25,978	10 3
	Contingent Liability—In connection with perpetual leases granted to Australian National Research Council and the Pharmaceutical Society of N.S.W.—Maximum Liability £901 16s. 8d.				
(902)					
<u>£32,981</u>				<u>£33,141</u>	<u>17 3</u>

ASSETS.

1946.			1947.		
£			£	s.	d.
344	Cash at Bank and in Hand			292	8 3
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—				
	Held for—				
	Clarke Memorial Fund	1,800	0	0	
	Walter Burfitt Prize Fund	1,000	0	0	
	Liversidge Bequest	700	0	0	
	Research Fund	3,000	0	0	
	General Purposes	4,360	0	0	
10,660				10,860	0 0
26	Prepayment			61	5 0
	Debtors for Subscriptions	97	14	0	
	Deduct Reserve for Bad Debts	97	14	0	
14,715	Science House—One-third Capital Cost			14,715	0 0
6,800	Library—At Valuation			6,800	0 0
393	Furniture—At Cost—less Depreciation			373	0 0
32	Pictures—At Cost—less Depreciation			30	4 0
11	Lantern—At Cost—less Depreciation			10	0 0
<u>£32,981</u>				<u>£33,141</u>	<u>17 3</u>

TRUST AND RESEARCH FUNDS.

	Clarke Memorial.	Walter Burfitt Prize.	Liversidge Bequest.	Research.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Capital at 28th February, 1946 ..	1,800 0 0	1,000 0 0	700 0 0	3,000 0 0
Revenue—				
Balance at 28th February, 1946	75 2 5	30 12 10	25 15 0	247 15 0
Interest for twelve months ..	64 13 9	34 15 0	25 15 0	99 5 0
	139 16 2	65 7 10	51 10 0	347 0 0
<i>Deduct</i> Expenditure ..	31 2 6	—	51 10 0	24 11 8
Balance at 28th February, 1947 ..	£108 13 8	£65 7 10	—	£322 8 4

ACCUMULATED FUNDS.

	£ s. d.
Balance at 28th February, 1946	25,774 18 6
Add Surplus for twelve months (as shown by Income and Expenditure Account)	255 1 9
	26,030 0 3
Less Increase in Reserve for Bad Debts	51 10 0
	£25,978 10 3

G. D. OSBORNE.

Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1947, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,

Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 21st March, 1947.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1946, to 28th February, 1947.

1945-6.		1946-7.	
£		£ s. d.	£ s. d.
492	To Printing and Binding Journal—Vol. 79	355 8 7	
310	„ Salaries	363 0 0	
145	„ Library—Purchases and Binding	124 16 7	
49	„ Printing—General	68 1 0	
171	„ Miscellaneous	102 8 7	
63	„ Postage and Telegrams	95 2 1	
42	„ Rent—Science House Management Committee	42 14 8	
37	„ Cleaning	39 17 6	
23	„ Depreciation	22 9 0	
19	„ Telephone	18 14 9	
15	„ Insurance	15 4 3	
12	„ Audit	12 12 0	
9	„ Electricity	8 7 9	
1	„ Repairs	—	
1,388			1,268 16 9
73	„ Surplus for Twelve Months		255 1 9
£1,461			£1,523 18 6

1945-6.		1946-7.	
£		£ s. d.	£ s. d.
478	By Membership Subscriptions		521 17 0
400	„ Government Subsidy		400 0 0
425	„ Science House—Share of Surplus		436 0 0
131	„ Interest on General Investments		144 19 4
13	„ Receipts from Reprints	65 2 0	
	Less Expenditure	59 3 2	
			5 18 10
1	„ Other Receipts		1 1 0
13	„ Proportion of Life Members' Subscriptions		8 0 0
	„ Annual Dinner—		
	Received	57 14 0	
	Less Expenses	51 11 8	
			6 2 4
£1,461			£1,523 18 6

The Annual Report of the Council (1946-47) was read, and on the recommendation of Dr. Bolliger, adopted.

REPORT OF THE COUNCIL, 1946-47 (RULE XXVI).

We regret to report the loss by death of three members since April 1st, 1946: Henry Gordon Farnsworth (1921), Sir George A. Julius (1911) and Carl Adolph Sussmilch (1901).

By resignation the Society has lost seven members: Jean Armytage, Una Black, Daphne Buckley, Ronald S. Clarke, E. A. Eastaugh, Arthur C. A. Flack and P. Hindmarsh.

The membership now stands at 314, 22 new members having been elected during the year, namely Gordon Alfred Barclay, Ernst Herbert Blaschke, Bruno Breyer, Keith Edward Bullen, Rodney Thomas Cook, Norma Winifred Donohoo, Felix Gutmann, Ernest John Jasper, Nora Hinder, Guy Frederick Johnson, Michael Lederer, John Charters McPherson, Helen May McRoberts, Albert May, Charles St. John Mulholland, Norman Pinwell, Bryce Harrison Potter, Cecil Rhodes-Smith, Beryl Scott, Ifor Morris Thomas, Margaret Crowley Weston and Norman Richard Wyndham.

Eleven ordinary meetings of the Council and two special meetings were held during the year commencing April 1st, 1946, at which the average attendance was 15. During the same period, nine general monthly meetings were held, the average attendance being 37.

Two special meetings of Council were held for the purpose of discussing the Society's objects. Many suggestions were made with a view to obtaining greater attendance at general meetings, and for a recognition of the Society's influence in the scientific world and in the community. It is expected that proposals arising from these discussions will be implemented in the near future.

Election of Councillor.—Miss Phyllis Rountree, B.Sc., Dip.Bact., was elected to the Council at the special Council meeting of August 7th, 1946, in place of Mr. P. Hindmarsh, who had resigned.

Twenty-two papers were accepted for reading and publication during the year, and the following short talks and lecturettes were given :

"Australian Gem Stones", by R. O. Chalmers, A.S.T.C.

"Synthetic Diamond", by D. P. Mellor, D.Sc., F.A.C.I.

"Some Recent Advances in Cellular Metabolism", by J. L. Still, M.Sc., Ph.D.

"New Instruments of Scientific Interest", by D. P. Mellor, D.Sc., F.A.C.I.

"Consciousness and Instinct", by A. S. Le Souef.

Film.—A film of the eruption of Ruapehu was screened.

Exhibit.—Exhibit and demonstration of the Geiger Counter was given by N. A. Faull, B.Sc., A.Inst.P.

Symposia.—At the monthly meeting of August 7th, 1946, a symposium on "Power Resources of the Commonwealth" was held, the following addresses being given :

"Fuel Energy", by J. A. Dulhunty, D.Sc.

"Solar Energy", by T. Iredale, D.Sc., F.R.I.C.

"Atomic Energy", by R. B. Makinson, B.Sc., Ph.D.

At the meeting of October 2nd, 1946, a second symposium was held, the subject being "Tracer Elements". The following addresses were given :

"The Production and Measurement of Radio-active Isotopes", by N. A. Faull, B.Sc., A.Inst.P.

"The Use of Radio-active Tracers in Biological Investigations", by W. P. Rogers, Ph.D.

Commemoration of Great Scientists.—The November meeting was devoted to the commemoration of great scientists, and the following addresses were given :

"Boucher de Perthes—The Antiquity of Human Culture", by Professor A. P. Elkin.

"Gottfried Wilhelm Leibnitz", by W. B. Smith-White, B.Sc.

"Tycho Brahe", by H. W. Wood, M.Sc.

"Valerius Cordus and the Pharmacopœia", by Dr. A. Albert.

Popular Science Lectures.—Five Popular Science Lectures were delivered in the months of May, July, August, September and October.

The lectures were much appreciated by members of the Society and the general public.

May 16th.—"Extinct Monsters", by H. O. Fletcher.

July 18th.—"A New Road for the Disabled Soldier", by Professor O'Neill.

August 15th.—"Recent Developments in Plastics", by A. R. Penfold, F.A.C.I., F.C.S.

September 19th.—"The Smallest Forms of Life—Virus", by P. M. Rountree, M.Sc., Dip.Bact.

October 17.—"Triumph over Pain—The Story of Anaesthesia", by Dr. W. I. T. Hotten.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1946 was delivered by Professor L. A. Cotton, M.A., D.Sc., on June 20th, 1946, the title being "The Pulse of the Pacific".

Clarke Memorial Medal.—The Clarke Memorial Medal was awarded to Mr. J. M. Black, A.L.S. (*honoris causa*), of Adelaide, in recognition of his distinguished contributions to natural science in Australia.

Liversidge Research Lectures.—The Liversidge Research Lectures were delivered by Dr. L. H. Briggs, D.Phil. (Oxon.), D.Sc. (N.Z.), at the Chemistry Department of the Sydney University on August 12th and 13th, 1946, the subject being "Plant Products of New Zealand".

Government Grant.—A grant of £400 was received from the Government of New South Wales. The Society greatly appreciates the Government's continued interest in its activities.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition. During 1946 £200 was invested in the Commonwealth Security Loan.

Royal Society, London.—Dr. Edgar Booth, of the International Wool Secretariat, and Mr. A. Maccoll represented the Royal Society of New South Wales at the commemoration celebrations in honour of Sir Isaac Newton, held in London, July, 1946.

Annual Dinner.—The Annual Dinner was held on March 27th, 1947, in the Withdrawing Room, Union Refectory, The University of Sydney. His Excellency Lieutenant-General John Northcott, C.B., M.V.O., Governor of New South Wales, and Miss Northcott were present, and the Minister for Education, the Honourable R. J. Heffron, represented the Premier and the State Parliament. A total of 81 members and friends were present. On this occasion the wives of guests were invited.

Science House.—The Royal Society's share of the profits in Science House during the period March 1st, 1946, to February 28th, 1947, was £436.

Science House Management Committee.—The Royal Society has had as its representatives at the meeting of the Management Committee of Science House Dr. G. D. Osborne and Mr. F. R. Morrison, and as substitute representatives Dr. J. A. Dulhunty and Mr. H. H. Thorne.

Pollock Memorial Fund.—On the recommendation of the Senate of the Sydney University the Council decided that the fund established in 1922 to perpetuate the memory of the late Professor J. A. Pollock, be placed in the Trust Fund of the University of Sydney. This Society is represented on the committee by the President, Mr. H. H. Thorne, Professor Vonwiller and the Honorary Secretary.

A.N.Z.A.A.S. Conference, Adelaide, August 20-27th, 1946.—Dr. A. Bolliger and Dr. G. D. Osborne were appointed as delegates to represent the Society.

Visit of the President to the United States of America.—Following the invitation to the President to nominate a representative of the Royal Society of New South Wales to attend the meetings of the National Academy of Sciences and the American Philosophical Society respectively, the President, Dr. F. Lions, was chosen by the Council to represent the Society. The meetings were held in Philadelphia and Washington from October 8th to 23rd, 1946.

During the absence of the President, Dr. A. Bolliger presided at meetings and undertook the duties of the President.

Sir Harold Spencer Jones.—The Astronomer Royal was welcomed by the Councils of the New South Wales Branch of the British Astronomical Association and the Royal Society of New South Wales, in the reception room of Science House, on Friday, February 21st, 1947, at 3.15 p.m. On the same evening, at 8 p.m., Sir Harold delivered a Popular Lecture entitled "Life on Other Worlds", in the Wallace Theatre, University of Sydney. The lecture was greatly appreciated by an audience of about 400 members of scientific societies and the general public.

Meeting of the Library Committee of Science House Owner Bodies.—The meeting was held on June 6th, 1946, to discuss the question of providing central library facilities for the owner bodies of Science House when building extensions envisaged had been effected. Although the three owner bodies were not in agreement regarding the merging of the separate libraries, unanimity was reached regarding provision of a common reading room.

The Library.—The amount of £38 19s. 1d. has been expended on the purchase of periodicals, and the amount of £82 17s. 6d. spent on binding; the total sum spent on the library over the past twelve months is therefore £121 16s. 7d.

Exchanges.—The number of volumes now being sent to other societies is 314.

Accessions.—For the twelve months ended February, 1947, the number of accessions entered in the catalogue was 2,177 parts of periodicals and 66 new books.

Borrowers and Readers.—Members and visitors reading in the library numbered 26.

The number of books and periodicals borrowed by members, institutions and accredited readers was 239.

Among the institutions which made use of the arrangements for inter-library borrowing were: Elliotts and Australian Drug Co., National Standards Laboratories, The Fisher Library, Sydney County Council, Australian Paper Manufacturers, Colonial Sugar Refining Co. Ltd., C.S.I.R., Canberra, Drug Houses of Australia, McMaster Laboratories, Siemens Australia Ltd., Amalgamated Wireless of Australia, Royal North Shore Hospital, Botanic Gardens and the Melbourne University.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member was read for the second time. The following person was duly elected a member of the Society: Raymond James Wood Le Fevre.

Election of Honorary Members.—The following were elected to honorary membership of the Society: Sir Harold Spencer Jones and Professor Frederick Wood Jones.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1947 to Dr. H. Lyman Clark.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1947 would be delivered by Professor H. S. Summers on July 17th.

Election of Auditors.—On the motion of Mr. R. S. Nyholm, seconded by Dr. J. L. Still, Messrs. Horley & Horley were re-elected as Auditors to the Society for 1947-48.

The retiring President, Dr. F. Lions, delivered his address entitled "The Freedom of Science".

At the conclusion of the address, Dr. Lions welcomed Dr. J. A. Dulhunty to the Presidential chair. The new President acknowledged the honour conferred upon him, and called upon Mr. Nyholm to propose a vote of thanks to the retiring President for his address and for his services to the Society during his term of office. This was carried by acclamation.

The following papers were read by title only: "The Orbit of H3494 ($2^h 15^m.6$, $-35^\circ 54'$: 1900)", by H. W. Wood, B.Sc.; "Note on the p-p'-Dinitro Diphenyl Disulphide", by G. K. Hughes and E. P. O'Leary; "Occultations Observed at Sydney Observatory during 1946", by W. H. Robertson, B.Sc.; "Dimensional Methods in the Design of Industrial Chemical Research", by R. C. L. Bosworth, Ph.D., D.Sc., F.A.C.I., F.Inst.P.; "Geology of the Ashford Coalfield", by F. N. Hanlon, B.Sc.; "A Magnetic Survey in the Vicinity of the Volcanic Neck at Dundas, N.S.W.", by F. N. Hanlon, B.Sc.

F. LIONS, President.

May 7th, 1947.

The six hundred and fortieth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Twenty-seven members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Lennard Robert Hall, James Charles Lloyd, William B. Smith-White.

Popular Science Lecture.—It was announced that the first Popular Science Lecture for 1947 would be given by Mr. W. H. Maze on Thursday, May 15th, at 8 p.m., and would be entitled "The Hunter River Valley—A Future T.V.A.?"

International Geological Congress.—It was also announced that the International Geological Congress would take place in London from August 25th to September 1st, 1948.

Library.—The following donations were received: 31 parts of periodicals and 77 back numbers.

Notice of Motion.—The President moved the following addition to the first paragraph of Rule V: "A copy of the list shall be posted to each financial member of the Society not less than ten days before the closing date for nominations."

The following papers were read:

"Studies in Semiquinones. Part I. p-Phenylenediamine and Benzidine Derivatives", by G. K. Hughes, B.Sc., and N. S. Hush.

"The Determination of Maximum Inherent Moisture in Coal by Controlled Vaporisation of Adherent Moisture", by J. A. Dulhunty, D.Sc.

The following paper was read by title only:

"A New Method of Approximating the Binomial and Hypergeometric Probabilities", by D. T. Sawkins, M.A. (Syd.), B.A. (Camb.).

The following papers read by title at the April general meeting were presented and discussed: "Dimensional Methods in the Design of Industrial Chemical Research", by R. C. L. Bosworth, Ph.D., D.Sc.

"Magnetic Survey in the Vicinity of the Volcanic Neck at Dundas, N.S.W.", by F. N. Hanlon, B.Sc., Dip.Ed.

Exhibit.—"Synthetic Minerals used in Optical and other Scientific Apparatus", by Miss F. M. Quodling, B.Sc.

Demonstration.—Dr. A. Bolliger gave a demonstration entitled "Some Photo-chemical Properties of Tungstic Acid".

June 4th, 1947.

The six hundred and forty-first General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Thirty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Charles Joseph Magee, Fritz Henry Reuter, Gregory Stewart Buchanan and Bruce Ritchie.

Popular Science Lecture.—It was announced that the second Popular Science Lecture for 1947 would be given by Mr. J. R. Kinghorn on Thursday, June 19th, at 8 p.m., and would be entitled "Snakes and Snake Venom".

Library.—The following accessions were received: 79 parts of periodicals and eight purchases.

Motion from Last Meeting.—The President moved the addition to the first paragraph of Rule V, notice of which had been given at the previous meeting, and announced that the proposed addition would be submitted for confirmation at the next general meeting.

The following papers were read:

"A Note on the Preparation of some o-Carboxy-Phenyl-Arsine Derivatives", by G. A. Barclay and R. S. Nyholm, M.Sc.

"The Colorimetric Estimation of Apomorphine", by E. R. Cole, B.Sc.

The following paper was read by title only:

"Theoretical Aspects of the Maximum Recovery in Absorption or Stripping Operation", by Geo. E. Mapstone.

Lecturette.—A lecturette entitled "Submarine Canyons, with special reference to recent discoveries off the South Australian Coast" was given by Dr. G. D. Osborne.

July 2nd, 1947.

The six hundred and forty-second General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Fifty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society: Ronald Louis Werner.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1947 would be delivered on Thursday, July 17th, at 8 p.m., by Professor H. S. Summers, and would be entitled "The Teachers of Geology in Australian Universities".

Library.—The following accessions were received: 218 parts of periodicals, three back numbers and 10 purchases.

Confirmation of Motion.—Addition to the first paragraph of Rule V. The President put the motion for its confirmation, which was carried.

The following papers were read:

"Possible Causes of Intraformational Disturbances in the Carboniferous Varve Rocks of Australia", by Rhodes W. Fairbridge, D.Sc., F.G.S. (Communicated by Professor L. A. Cotton.) Dr. G. D. Osborne contributed supplementary remarks on the paper.

"The Oxidation Potentials of the Tris 1, 10 Phenanthroline and Tris 2, 2' Dipyridyl Ferrous Ions", by F. P. Dwyer, D.Sc., and H. A. McKenzie, M.Sc.

"A Note on the Instability Constant of the Tris 2, 2' Dipyridyl Ferrous Ion", by F. P. Dwyer, D.Sc., and H. A. McKenzie, M.Sc.

Films.—The following films which had been made available through the good offices of Mr. R. S. Nyholm were screened:

1. "The Body Defences against Diseases."
2. "The Action of the Kidneys."
3. "Fuels and Heat."
4. "Light Waves and their Uses."

August 6th, 1947.

The six hundred and forty-third General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. J. A. Dulhunty, was in the chair. Twenty-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

Popular Science Lecture.—It was announced that the third Popular Science Lecture for 1947 would be given by Dr. R. L. Aston on Thursday, August 21st, at 8 p.m., and would be entitled "Measuring the Face of a Continent—the Use of Radar and Photography in Mapping".

Monographs.—The President also announced that an Editorial Sub-committee had been appointed with a view to publishing one or two monographs per annum.

Library.—The following accessions were received: 261 parts of periodicals, 13 purchases, 453 back numbers and two books.

The following papers were read :

"The Colorimetric Determination of Iron in Canned Foods with 1, 10 Phenanthroline", by H. A. McKenzie, M.Sc.

"The Reaction of Pyridine with Dichlorotetrammine Cobalt (III) Complexes", by J. A. Friend and D. P. Mellor, D.Sc.

"A New Method for the Comparison of the Thermal Conductivities of Fluids. Part I", by R. C. L. Bosworth, Ph.D., D.Sc.

The following papers were read by title only :

"The Uniform Convergence of Sequences in Monotonic Functions", by F. A. Behrend, D.Sc.

"A Method of Determining the Distribution of Oil in a Reservoir Rock by Means of Ultra-Violet Light", by L. C. Noakes, B.A.

Lecturette.—A lecturette entitled "Some New American Research Tools" was given by Dr. F. Lions.

September 3rd, 1947.

The six hundred and forty-fourth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Thirty members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Adrian Noel Old, Gladys Olive Conabere, Nancy Evelyn Ray and Reginald John Ray.

Popular Science Lecture.—It was announced that the fourth Popular Science Lecture for 1947 would be delivered by Mr. R. M. Gascoigne on Thursday, September 18th, at 8 p.m., and would be entitled "The Colouring Matter of Plants".

Library.—The following accessions were received : 102 parts of periodicals, 13 purchases, 40 back numbers and one book.

The following paper was read :

"Spectroscopic Characteristics of Ordinary Acheson Graphite", by K. B. Mather. (Communicated by Professor O. U. Vonwiller.)

The following papers were read by title only :

"The Petrology of the Silurian Volcanic Sequences at Wellington, N.S.W.", by M. J. Colditz, M.Sc.

"Studies in the Inheritance Resistance to Rust of Barley, I, II, III", by W. L. Waterhouse, M.C., D.Sc.

Discussion.—A discussion on Nuclear Science was held and the following short addresses were given :

"Stellar Energy", by H. W. Wood, M.Sc.

"Separation of Isotopes by Gaseous Diffusion", by R. C. L. Bosworth, Ph.D., D.Sc.

"Radioactive Tracers in Chemistry", by F. Lions, B.Sc., Ph.D.

October 1st, 1947.

The six hundred and forty-fifth General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Thirty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Alan M. Downes, Naida S. Gill, Stuart F. Gill, Leo Edmund Maley.

Popular Science Lecture.—It was announced that the fifth Popular Science Lecture for 1947 would be given by Dr. H. R. Poate on Thursday, October 16th, at 8 p.m., and would be entitled "The Story of Goitre".

Conversazione.—It was also announced that, following a letter received from the Emergency Committee of Atomic Scientists, U.S.A., signed by Albert Einstein, regarding Atomic Education, the Society would hold a *Conversazione* in the Great Hall, University of Sydney, on Wednesday, October 8th, at 8 p.m. Exhibits from the various departments of the University and the C.S.I.R. would be open for inspection, and would be followed by short addresses, which would be delivered by His Excellency the Governor of New South Wales, Lieut.-General John Northcott, C.B.,

M.V.O., the Minister for Education, the Honourable R. J. Heffron, the Chancellor of the University of Sydney, Sir Charles Bickerton Blackburn, and the Acting President of the Society, Dr. Francis Lions.

Library.—The following accessions were received : 179 parts of periodicals, four purchases and 115 back numbers.

The following papers were read :

“ Corrosion of Surfaces Heated above the Boiling Point of the Corrodant ”, by R. C. L. Bosworth, Ph.D., D.Sc.

“ A New Method for the Comparison of the Thermal Conductivities of Fluids. Part II ”, by R. C. L. Bosworth, Ph.D., D.Sc.

Lecturettes.—The following lecturettes were given :

“ Palaeontological Work in the U.S.A. ”, by Dr. Ida Brown.

“ Impressions of Chemical Research Activity in Britain ”, by Dr. T. Iredale.

November 5th, 1947.

The six hundred and forty-sixth General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Forty-three members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of five candidates for admission as ordinary members of the Society were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Arthur S. Ritchie, Patrick R. McMahon, Peter Nordon.

Library.—The following accessions were received : 221 parts of periodicals, 204 back numbers and four purchases.

Sidey Summer-time Medal.—The Acting President, Dr. F. Lions, on behalf of the Royal Society of New Zealand, after a brief summary of the history of the award, presented the Sidey Summer-time Medal to Dr. D. F. Martyn, of the Commonwealth Observatory, Mount Stromlo, Canberra.

The award was made to Dr. Martyn for his work on radar and the reception of radio waves from the sun.

The following papers were read by title only :

“ The General Geology of the Bombala District ”, by H. M. McRoberts, B.Sc.

“ The Geology of the Stanhope District, N.S.W. ”, by B. Scott, B.Sc.

Commemoration of Great Scientists.—The meeting was devoted to the commemoration of great scientists, the following addresses being given :

(1) “ Torricelli. ”

“ Helmholtz ” : Enunciation of the Principle of the Conservation of Energy, by Mr. J. B. Thornton.

(2) “ Semmelweis ” : Prevention of Puerperal Fever.

“ Simpson ” : Introduction of Chloroform Anæsthesia. (Illustrated with lantern slides), by Dr. K. Brown.

December 3rd, 1947.

The six hundred and forty-seventh General Monthly Meeting of the Royal Society of New South Wales, was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Acting President, Dr. F. Lions, was in the chair. Twenty-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of five candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Peter Beckmann, Neil E. Goldsworthy, Justin R. Humpoletz, George E. Mapstone, Gordon K. Webb.

Arnold Reymond Prize, 1951.—It was announced that a circular had been received from the University of Lausanne inviting applications for the award of the Arnold Reymond Prize, 1951.

Library.—The following accessions were received : 101 parts of periodicals, 209 back numbers and 10 purchases.

The following papers were read :

- "The Chemistry of Bivalent and Trivalent Rhodium. Part X. The Oxidation of Cæsium Hexachloro-Rhodate (III) to Cæsium Hexachloro-Rhodate (IV)", by F. P. Dwyer, D.Sc., R. S. Nyholm, M.Sc., and L. E. Rogers, M.Sc.
- "The Chemistry of Osmium. Part III. Complexes of Tertiary Arsines with Bivalent and Trivalent Osmium Halides", by F. P. Dwyer, D.Sc., R. S. Nyholm, M.Sc., and B. T. Tyson.
- "Geology of the North-Western Coalfield, N.S.W. Part I. Geology of the Willow Tree District", by F. N. Hanlon, B.Sc.
- "Geology of the North-Western Coalfield, N.S.W. Part II. Geology of the Willow Tree-Temi District", by F. N. Hanlon, B.Sc.
- "Geology of the North-Western Coalfield, N.S.W. Part III. Geology of the Murrurundi-Temi District", by F. N. Hanlon, B.Sc.
- Mr. Hanlon's papers were discussed by Dr. G. D. Osborne, who stated that the subject of the papers was very important from the viewpoint of (1) stratigraphy and (2) structural history at the end of the palæozoic era.
- "The Colorimetric Estimation of Strychnine", by E. R. Cole, B.Sc.
-

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Mr. C. St. J. Mulholland.

Honorary Secretary : Mr. R. O. Chalmers.

Meetings.—Five meetings were held during the year, the average attendance being seven members and four visitors.

April 18th.—Address by Mr. L. Owen on "Some Aspects of Australian Coal". Exhibit by Mrs. K. M. Sherrard : *Corynoides* c.f. *calicularis*. This form is placed by Ruedemann among *formae incertae sedis*. It has not been recorded in Australia previously. It was found in black slates in the Shoalhaven Gorge near the mouth of Bungonia Creek and occurs with *Climacograptus bicornis* and its varieties, *Cryptograptus tricornis* and *Mastigograptus*.

June 20th.—Address by Dr. G. D. Osborne on "Evolution of the Structure and Physiography of the Sydney Basin".

September 19th.—Notes and Exhibits : By Miss Quodling : (a) Specimen of banded breccia from Hornsby ; (b) Specimen of gold in calcite from Hornsby. By Dr. Osborne : Andradite-wollastonite rock from the Oberon District. By Mr. Chalmers : Specimens of new minerals as yet undescribed, duplexite and bowleyite from Londonderry, near Coolgardie, Western Australia. Both are beryllium minerals. By Mr. Fletcher : A pseudo-fossil from Thudungara, N.S.W.

November 21st.—Meeting abandoned because of insufficient attendance.

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FOR

1948

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Parts I-IV

EDITED BY

W. B. SMITH-WHITE, M.A., B.Sc.

Honorary Editorial Secretary

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NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ _____ to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within _____ calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.]

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

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PRESIDENTIAL ADDRESS

By J. A. DULHUNTY, D.Sc.

Delivered to the Royal Society of New South Wales, April 7, 1948.

PART I. GENERAL.

Ladies and Gentlemen,

It is with great pleasure, after a year's careful observation of the inter-relationships of the Royal Society of New South Wales with the international community of science on the one hand, and the people of our own community on the other, that I can report confidently on the steady progress of our Society. I think it is fair to say that that Society stands as high today as ever it did in the public esteem, and that the increasingly wide circulation of our journal—it has increased about 23 per cent. during the year—is evidence that the published accounts of researches contained therein are of considerable interest in the world of Science.

During the year 35 original papers were accepted for reading and publication, the subject matter lying in many different branches of science. This is almost a 60 per cent. increase over the number of papers published in each of the last two years, and it would seem that the "spate of papers" anticipated by Dr. Lions last year might well be commencing to eventuate. Already there are distinct signs that there will be an even greater number of papers for publication in the year now commencing. It might well be expected that the new *Australian Journal of Research* to be published under the ægis of the Council for Scientific and Industrial Research will reduce the number of communications to the Royal Society, but there is no evidence as yet of any such effect.

Early in the Society's year the newly appointed Governor-General of the Commonwealth of Australia, the Right Honourable W. J. McKell, P.C., was graciously pleased to accept the office of Patron of the Society, and the Society was honoured by his presence, together with that of his daughter, Miss Betty McKell, at the Society's Annual Dinner in the Refectory of the Sydney University Union on April 1st, 1948. The Society was also honoured by the presence of its old friend the Minister for Education, the Honourable R. J. Heffron, and Mrs. Heffron, and of the Vice-Chancellor of the University of Sydney, Dr. Stephen Roberts, and Mrs. Roberts and several distinguished representatives of sister societies. Altogether, 110 members and guests attended the function which was considered an outstanding success.

During the year, despite the loss of six members by resignation, the Society's ordinary membership gained by nineteen, twenty-five new members being elected during the year. It is a great pleasure for me to be able to record that gain, and to note that death claimed none of our members during this past year. Also, it is a pleasure to record that our list of Honorary Members has been increased by the election of two very distinguished scientists, Sir Harold Spencer Jones, F.R.S., and Professor F. Wood-Jones, F.R.S.

A—April 7, 1948.

The ordinary monthly meetings of the Society have been well attended. In addition to the reading of papers several short addresses and lectureries have been given: "Submarine Canyons, with special reference to recent discoveries off the South Australian Coast", by Dr. G. D. Osborne; "Some New American Research Tools", by Dr. F. Lions; "Palaeontological Work in the U.S.A.", by Dr. Ida Brown; and "Impressions of Chemical Research Activity in Great Britain", by Dr. T. Iredale. The September meeting was devoted to a short Symposium on Some Aspects of Atomic Science, addresses being given by Mr. H. W. Wood ("Stellar Energy"), Dr. R. C. L. Bosworth ("Separation of Isotopes by Gaseous Diffusion"), and Dr. F. Lions ("Radio-active Tracers in Chemistry"). The July meeting was largely given up to a screening of sound films, whilst at the November meeting the Society's customary practice of commemorating great scientists was followed, Mr. J. B. Thornton delivering an address on Torricelli and Helmholtz, whilst Dr. K. Brown discussed the work of Semmelweis and Simpson.

The usual five Popular Science Lectures were delivered during the months of May, June, August, September and October, and were well attended and greatly appreciated, both by members of the Society and by the general public. The subjects were "The Hunter River Valley—A Future T.V.A.?" by Mr. W. H. Maze; "Snakes and Snake Venom", by Mr. J. R. Kinghorn; "Measuring the Face of a Continent—The Use of Radar and Photography in Mapping", by Dr. R. L. Aston; "The Colouring Matters of Plants", by Mr. R. M. Gascoigne; and "The Story of Goitre", by Dr. H. R. Poate.

The Clarke Memorial Lecture was delivered in July by Professor H. S. Summers, D.Sc., on the subject "The Teachers of Geology in Australian Universities", and was of great personal interest to geologist members of the Society.

The Clarke Memorial Medal this year was awarded to Dr. A. B. Walkom, D.Sc., for his distinguished contributions to palaeobotany, and I am sure that every member of the Society rejoices at this award to so old a friend of science and so distinguished a member of this Society as Dr. Walkom.

The time for the award of the Walter Burfitt Prize came round again during this year and the Council had considerable difficulty in making its selection. An important principle was established during the discussions to the effect that the Walter Burfitt Prize should only be awarded once to the same investigator. The Prize was eventually awarded to Dr. J. C. Jaeger, a graduate of the Universities of Sydney and Cambridge, at present resident in Tasmania, for his distinguished contributions to the science of mathematics.

This year too, for the first time, the James Cook Medal has been awarded. Members will remember that some few years ago an old esteemed life member of our Society, Mr. H. F. Halloran, made funds available to the Society for the founding of two medals to be awarded annually. The senior one of these, the James Cook Medal, is to be awarded for outstanding contributions to Science and human welfare in the southern hemisphere, and the other, the Edgeworth David Medal, is to be awarded to a younger scientist for outstanding contributions to learning. The distinguished first recipient of the James Cook Medal is Field-Marshal the Right Honourable Jan Christian Smuts, Prime Minister of the Union of South Africa. I am sure I express the pleasure of all members at our ability thus to show our appreciation of Field-Marshal Smuts and of his work, and to say that our Society is honoured by his acceptance of the award. The first award of the Edgeworth David Medal will probably be made during the forthcoming year.

Quite early in our year the Council received communications from the Association of Atomic Scientists, and the Emergency Committee of Atomic

Scientists, headed by Professor Albert Einstein, urging the Royal Society of New South Wales to do whatever it could in the work of educating the non-scientific community against atomic warfare. After some deliberation the Council decided to hold a *Conversazione* in the Great Hall of the University and to open its campaign by having some short addresses delivered during the evening. The function was duly held early in October and was well attended by members and their guests. The Society's distinguished Patron, His Excellency the Governor of New South Wales, Lieutenant-General John Northcott, C.B., M.V.O., who has had first-hand experience of the results of atomic bombing in Japan, delivered the first address, and was followed by the Chancellor of the University, Sir Charles Bickerton Blackburn, the Minister for Education, the Honourable Mr. R. J. Heffron, and the Acting President of the Society, Dr. F. Lions. The atomic education campaign is to be advanced still further in the near future by the Society.

It is gratifying to record that the finances of the Society remain in a healthy state, even though the accounts show a slight loss on the year's working. This has long been anticipated by the Council as a result of the "backing up" of printing for the Journal. It has, however, to be recognized that the rapid rise in the costs of printing in the last year or so seriously threatens the stability of the Society's finances, and it is worthwhile pointing out to members again the importance of a greatly increased membership of the Society.

During the year the Society had the opportunity of entertaining at afternoon tea some distinguished visitors from abroad—Dr. E. H. Booth, of the International Wool Secretariat, in April, 1947; and Professor Raymond Firth, of the University of London, in March of this year. The Society is adopting a deliberate policy of endeavouring to entertain distinguished visiting scientists whenever they are in Sydney, and the opportunity affords, and thus enabling members to meet them informally.

At the November monthly meeting the Society had the opportunity of extending one of those courtesies to a sister academy which helped so much to build the international brotherhood of science. At the request of the President of the Royal Society of New Zealand the Sidey Summer-time Medal was presented by the Acting-President to Dr. D. F. Martyn of the Mount Stromlo Observatory for his work on radar and the receipt of radio waves from the sun.

The library continues to expand and many of the gaps on our shelves because of the war have now been filled. I should like to take this opportunity to express not only my own but also the Society's sincere thanks to our Honorary Librarian, Mr. H. W. Wood, for the excellent work he has done in the library this year.

During the early part of my term of office as President it became necessary for me to proceed abroad at short notice in order to extend my studies on coal utilization. The Council granted me leave of absence, and Dr. Lions agreed to act and was appointed Acting-President for the remainder of the year or until I should return. Much of the work that usually falls to a President has consequently fallen on his shoulders, and I should like here to express my thanks to him for so willingly carrying on. It is also in order for me here, also, to say just a few words in appreciation of the work of the other members of my executive, who are all retiring from their executive positions this year. First, Dr. Mellor has been the Editorial Secretary of the Society for a good many years now. It is to his wholehearted and enthusiastic work that the Society owes much of the esteem in which its Journal is held abroad. His modernization of its format has saved the Society very considerable expense, and his careful editing has helped in securing and maintaining the present high standard of our Journal. The Society will always owe to Dr. Mellor a very great debt of gratitude.

Then, although Dr. Osborne, our retiring Honorary Treasurer, and Mr. Morrison, our retiring Honorary Corresponding Secretary, have not had such a long period of service as Dr. Mellor, they have done excellent work for the Society, and I do want to tell them that that work is very greatly appreciated.

I come now to the second part of my address.

PART II. SOME NEW HORIZONS IN COAL UTILIZATION AND RESEARCH.

The structure of modern civilization has evolved in such a way that it now depends on fuel-energy, derived from coal and petroleum, for practically all its activities. Its needs have become so great that the value of coal and petroleum produced each year represents almost half the total value of all mineral production. This trend is progressing more rapidly as time goes on, and it appears highly probable that it will continue to do so during the next century of progress, resulting in a steadily increasing demand for energy now obtained from coal, petroleum and natural gas.

Scientists and technologists are faced at present with difficult problems regarding the future of the coal industry in relation to world requirements of fuel-energy, and questions of utilization, conservation of resources, and planning of research are receiving a great deal of attention in the principal coal-producing countries of the world.

COAL CONSUMPTION AND POWER REQUIREMENTS.

Looking back over the last one hundred years, progress and expansion of industry and transport resulted in a rapid increase in world production of coal up to about 1910, when it reached approximately 1,200 million tons per annum. Since then industry and transport have continued to expand and grow at a greater rate than during the latter half of the nineteenth century, but production of coal has increased but little, remaining at about 1,300 to 1,400 million tons. It follows that consumption has remained more or less constant for about 40 years, although demands for fuel-energy have increased very considerably. This appears to be a consequence of two major factors—more economic utilization of coal, and the contribution of petroleum to world requirements of fuel-energy.

Petroleum has met rapidly increasing demands for fuel in transport on the land and in the air, and also on the oceans where firing with fuel oil has largely replaced the use of coal. It has supplied some of the growing demands for stationary steam-raising plants and domestic heating, but its contribution in this respect represents only a small portion of increased requirements for heavy industry, gas production, generation of electrical power and railway transport, all of which depend almost entirely on coal. The fact that increased demands in these fields have not resulted in greater consumption of coal is evidence of successful application of results of scientific and engineering research to problems of fuel-economy. Overall efficiency of steam-raising plants and power units has risen considerably; improvements in furnace efficiency have played an important part; the use of gas and electricity for domestic and many industrial purposes, in place of solid fuel, has substantially reduced the amount of energy wasted or lost in using coal; and important improvements have been made in industrial practice where coal or coke is used to supply heat for processing, as well as carbon, as in the case of the steel industry.

Looking into the future, it is generally believed that a great deal more economy is yet to be effected in the use of coal, and of gas and electrical power derived from it, and that consumption is not likely to increase appreciably while ample supplies of petroleum are available to meet rapidly increasing

demands for liquid fuel. Unfortunately, reserves of petroleum are limited, and uncertainty regarding its useful life, and the extent to which coal may be called upon in the future to meet requirements now supplied by petroleum, gives rise to problems of a difficult nature.

It is not possible to assess the life of petroleum reserves in terms of a definite number of years, as they are unlikely to become exhausted at any particular stage. New fields are being developed as time goes on, and enormous reserves almost certainly remain to be discovered in the crust of the earth. Statistics show, however, that old fields are being used up more rapidly than new fields are being discovered. This means that an increase in production, at any time in the future, will result in a subsequent decrease below present day figures until available reserves are restored by development of new fields. Improved technique, and greater efforts by petroleum geologists and engineers in the development of new fields, will no doubt speed up the rate at which new fields are made available in the future, but this advantage will probably be more than offset by increases in annual consumption of liquid fuel. It appears, therefore, that a world shortage of petroleum is inevitable in the future, although oil wells will continue to flow for many years to come.

It is difficult to forecast when a permanent shortage will develop as a result of the excess rate at which old fields are being exhausted. It will probably commence to be felt very soon, in fact it is even possible, if not probable, that shortages of petroleum products at present existing in many countries may never completely disappear but will gradually become permanent. The present shortages are not due entirely to international economic difficulties, but rather to the fact that present-day consumption of liquid fuel is so great that production is unable to meet demands. During the present winter, a temporary peak in consumption has made it necessary for the United States to cancel all exports of petroleum products to enable her to carry on with minimum supplies, although production of oil in that country at present represents an all-time record.

To the scientists and economists responsible for planning utilization and development of national fuel resources, the existing situation presents many strange problems and uncertainties. If the present rate of consumption of coal continues to remain more or less constant, as it has for the last forty years, the coal resources in most countries represent considerable reserves. If, however, deficiencies in fuel-energy, due to permanent and increasing petroleum shortages, are to be met by additional consumption of coal, reserves immediately assume much smaller proportions, particularly with respect to special types of high-grade coals. Such questions lead to philosophical speculation and they are difficult to answer with any degree of certainty; however the time has arrived when they must be given serious consideration.

Methods of producing liquid fuel from coal by hydrogenation, or complete gasification and hydrocarbon synthesis involving principles of the Fischer-Tropsch process, are well established and were practised on a large scale in Germany before and during the war. Large quantities of oil and petrol can be produced from coal, but the processes are complicated, requiring enormous outlays in specialized and expensive plant, and cost of production is relatively high. In fact, the production of large quantities of oil from coal could be regarded as an outstanding achievement in industrial chemistry, rather than a simple and economical way of meeting the world's liquid fuel requirements. Furthermore, it would consume large amounts of coal of which reserves are not unlimited. In view of these facts the necessity to depend on coal oil in place of petroleum, so simple and economically obtained, would in some ways seem to be a retrogressive step which may even hinder or modify trends of modern progress in industry and transport. It is difficult to imagine that such a change could take

place. In the past, when facilities have become inadequate for the requirements of advancing civilization, ingenuity and inventive skill always seem to have provided new and more efficient facilities, helping to forward progress rather than retard it. If such philosophy is sound, and if the approaching petroleum shortage really constitutes the failure of a facility to meet the requirements of modern progress, then it would appear reasonable to predict that some new source of energy may be made available in the near future to do the work which has proved too great for liquid and solid fuels. Perhaps this is already heralded in recent discoveries of release of atomic energy and in the intensive research on its utilization now being undertaken. Relatively small resources of the particular forms of uranium, so far used, have been sighted as possible limiting factors in the widespread use of atomic energy. However, in view of results obtained from research in nuclear physics during the last twenty years, the release of energy from all radio-active elements would not be an unreasonable expectation in the near future. In fact, the ultimate achievement of releasing energy from non-radio-active elements, of unlimited abundance, would not be any more fantastic at this stage than present accomplishments appeared only twenty years ago.

The way in which atomic energy could be used to replace all solid and liquid fuels is as yet obscure, but it is not difficult to visualize the normal sequence of events which could lead to such an end. Unfortunately the majority of nuclear physicists are still engaged in researches other than those directed towards everyday use of atomic energy, but some work is being done on the development of experimental plants for generation of electrical power. The successful operation of such plants may eventually save enormous quantities of coal at present used in supplying electricity for industrial, domestic and transport purposes. Furthermore, the availability of electricity wherever required would encourage the existing tendency to change over from the direct use of coal to the use of electrical power and heating, and thus conserve additional quantities of solid fuel. In this way it appears as though the first applications in the general use of atomic energy may relieve consumption of coal more than petroleum. However, with the more general use of electricity, petroleum now used for diesel power and domestic heating would be conserved, and eventually smaller atomic energy plants for steam-raising may possibly be adapted to large passenger and cargo ships now traversing the oceans of the world and consuming as much as one ton of fuel oil per mile. Such advances would conserve petroleum products for use in air and road transport, and future research in the transmission of electrical power may even provide facilities for the use, in these fields of transport, of electricity generated at large atomic power stations.

In view of the possibility of atomic energy eventually effecting a large reduction in consumption of coal, questions arise concerning the future of the coal industry. It appears most unlikely that coal will lose its status in the mineral industry. It already holds an important place in the chemical industry, indirectly supplying, through by-products of the gas and coking industries, raw materials for an almost endless variety of products. Many of these, such as the plastics, are rapidly becoming essential commodities of everyday life, and will continue to be used more extensively in the future. Demands for raw materials in the "synthetic" industries are already so great that supplies of by-products from coal carbonization are rapidly becoming inadequate and research is being carried out, in England and America, on production of raw materials directly from coal in much larger yields than obtained by carbonization. The most promising results have been obtained by alkaline oxidation of coal, using air, or oxygen, under pressure and at slightly elevated temperatures. Mixed organic acids produced in this way, and suitable for use in the chemical industry, represent as much as 60% by weight of the coal oxidized, and their value over and above probable cost of production far exceeds that of coal as a

fuel. Other investigations are being undertaken on specialized forms of solvent extraction, and chemical interaction between the "coal molecule" and various reagents, with the object of producing substances of more complex nature, and varied use in chemical manufacture, than organic acids from oxidation.

Recent advances have also been made in the manufacture of industrial carbons and low-priced structural materials for building and engineering construction. This work, which promises to open a new and important field of coal utilization, has been developed in the laboratories of Powell Duffryn Technical Services Ltd., England, and commercial production is already being undertaken. The processes involve pressure-moulding of very finely powdered coal followed by slow carbonization. This is so controlled that polymerization, associated with thermal decomposition, proceeds more rapidly than evolution of volatiles, which, together with development of plasticity during coking, results in a hard, fine-grained, carbonaceous product possessing the form into which the original powdered coal was moulded. The materials have many useful properties previously found in more expensive products made from graphite on one hand and thermo-hardening resins on the other, and they are almost certain to find a wide range of application in the future.

Such trends in coal utilization may well promote coal to a raw material of greater value than it now represents as a fuel, and belie fears for the coal industry should atomic energy eventually replace solid fuels to any appreciable extent.

Considerable progress has been made, over a number of years, in the use of pulverized coal for steam-raising in power stations and other large units, and it has extensively replaced stoker-fired furnaces in stationary plants in many countries. Rapid progress is now being made in research on the use of pulverized fuel in gas turbines and jet propulsion, in both stationary and mobile units. This technique eliminates steam-raising and steam-powered engines in the process of obtaining motive power from coal. It involves burning of powdered coal to produce high-velocity gases which pass over turbine blades providing power directly from energy released during combustion of the coal. Gas turbines offer certain advantages in stationary plants but their use is not likely to increase overall efficiency of energy transformation. In mobile units, such as railway locomotives, a very substantial increase in efficiency is indicated. In American projects, in which experimental gas turbine locomotives are already making test runs, an overall efficiency of about 15% to 17% is claimed, representing approximately twice the efficiency of steam powered railway engines. In the experimental locomotives coal is powdered on the engines by placing it under compressed air and then releasing pressure suddenly, which results in disintegration of the coal particles by a "bursting" effect. The locomotive is actually driven by electric motors powered from generators coupled to the turbines.

The use of gas turbines promises to increase the efficiency of coal utilization in railway transport by as much as 100%. This would constitute an important step in the contribution of research to more economical use of coal, mentioned earlier as a major factor in keeping annual consumption of coal more or less constant for the last forty years, although demands for fuel energy have increased continuously.

The foregoing speculations regarding deficiencies in adequate petroleum resources, and the use of atomic energy gradually replacing present-day fuels, may appear somewhat vague and unrealistic, but they must be taken into consideration in planning long-term programmes for fuel economy and research. Truly fundamental research, usually carried out in universities or institutions where work can proceed independently of immediate industrial requirements, need not be directly influenced by existing and likely future trends in coal utilization. It must continue so as to provide a fund of new knowledge about

coal for use as required by changing economic and industrial conditions. Fundamental research of this nature is best guided by experience in recognizing problems arising out of recent results and planning investigations along lines most likely to supply data which can be assembled to produce significant results. Applied research, including fundamental work undertaken to provide a result needed for immediate application, must be planned with respect to current problems and probable future developments in industry. It is in this field that scientists and technical authorities are faced with rapid and far-reaching changes already commencing to appear in coal utilization. Problems arise regarding relative urgency of work on projects such as combustion of coal in grate-fired boilers, as powdered fuel, or in gas turbines; widening the range of coal types used for particular purposes to meet dwindling, or unfavourably distributed reserves; production of liquid fuel from coal on a scale proportional to a country's total requirements; greater fuel economy in any particular industry; or conservation of special coal types which may be required for future industrial developments.

During the recent nationalization of the coal industry in the United Kingdom, a careful scientific survey was carried out by the Department of Scientific and Industrial Research to obtain data showing reserves of coals required for various purposes such as production of gas, domestic coke, metallurgical coke; and for domestic heating and steam raising in power stations and railway locomotives. The survey was based on data accumulated by the Geological Survey and Coal Survey over a number of years, and information from all colliery holdings obtained for purposes of assessment during the nationalization of the mines. In interpreting results it was assumed that research would continue to improve efficiency in utilization, as it had in the past, and that no great increases in consumption of coal were likely in the near future, although expansion in both domestic and industrial usage was almost certain. On this basis it was shown that reserves of all kinds of coal in the United Kingdom were ample for the next one hundred years at least. As a consequence of this finding, a general policy, although not officially stated, appears to have been adopted that there is no urgent need for drastic measures restricting the use of certain kinds of coal, or for intensive research programmes in fuel economy in addition to those already being undertaken. This would seem to bear special significance in view of the fact that one hundred years is a very short period of time in relation to the history of British industry, and to the nation's future progress. It suggests that authorities in a position to judge believe atomic energy will be used, probably in electrical power generation, so extensively in one hundred years time that coal, as a fuel, will not be of the same national importance as it is today. Electricity is at present replacing gas and solid fuel for all domestic purposes, and is taking the place of steam power in industry and railway transport, so rapidly that coal consumption will be reduced very considerably as soon as atomic energy is used in large power stations, as would seem to be its first and logical point of application.

No special programmes of research, or technical development, are being launched in the United Kingdom to meet the world shortage of petroleum, which appears imminent in the near future. England is accustomed to depending on external supplies of petroleum, and large reserves in the Middle East will probably be available longer than America's internal supplies. Furthermore, it is realized in England that processes such as hydrogenation and Fischer-Tropsch synthesis are available if, and when, required and that oils and petrol produced in this way are at present relatively expensive owing to high cost of coal production. In view of this it is felt that the most useful contribution to production of liquid fuels is first to reduce the cost of producing coal, by improved and more efficient mining technique, thus serving the dual purpose of providing industry with cheaper fuel as well as lowering the cost of liquid fuels from coal

if their production should become necessary. This does not mean that research on production of liquid fuel has been neglected in England. A great deal of fundamental work on principles involved in Fischer-Tropsch and hydrogenation processes has been carried out at the Greenwich Fuel Research Station and other places, and work on Fischer-Tropsch synthesis is being continued. Large-scale production of petrol from coal by hydrogenation was carried out by Imperial Chemical Industries Ltd., at Billingham-on-Tees, before the recent world war, and large quantities of aviation fuel were produced in their plant during the war by hydrogenation of creosote oil from the gas and coking industries.

In America it is considered that demands for liquid fuel are increasing so rapidly, and shortages of petroleum are so advanced, that production of liquid fuels from coal will be necessary in the very near future to relieve consumption of petroleum products upon which the country's economy and progress largely depend. As a result of this situation, and reluctance to rely on imported oils, large funds are being made available from government as well as private sources for the establishment of commercial scale plants to produce liquid fuels from coal, and also investigate improvements and modifications in the processes. In addition, preparations are being made to synthesize petrol from natural gas by a modification of the Fischer-Tropsch process, and attention is being paid to production of oil from oil shales of which there are very large reserves, but coal is regarded as the main source of future internal supplies of liquid fuel. The country is fortunate in possessing large reserves of coal which would certainly provide all requirements of both solid and liquid fuels for several hundreds of years to come. Both hydrogenation and Fischer-Tropsch plants are being developed, and important improvements are claimed in the latter. It is anticipated that it will be possible to produce petrol at a little less than twice the cost of refinery petrol, using coal costing ten to fifteen shillings (sterling) per ton.

COAL RESEARCH.

During the last 50 to 60 years a great deal of progress has been made in geological, chemical and physical research on the occurrence and nature of coal ; in mining engineering on production of coal ; and in fuel technology and industrial chemistry on its utilization. Work in all these fields has been stimulated by the fundamental importance of coal in industry and national economy, and by increasing demands for larger quantities of coal and for more efficient and varied utilization, which have provided a wide range of problems requiring urgent investigation.

Field Geology.

Early in the development of a coalfield, field geology plays an important part in revealing occurrence of coal and its distribution beneath the surface. Areas of coal-bearing strata are located, and surveys are carried out to produce geological maps and sections showing outcrops of the coal measures and their underground extensions, depths beneath the surface, and varying thicknesses. As data from bores and shafts become available, more detail surveys are carried out to determine variations in thickness of individual seams, and the general nature of underground structures such as regional folds and faults. Having carried this work as far as available data will permit, field geology is able to assist and advise when faults and other irregularities are encountered in mining operations, but there is a tendency to feel that there is not a great deal more it can do to help coal production in the established coalfield. Recent work, however, has shown that field geology can serve an important purpose even in well-developed coalfields. By a detail study of underground structure it is

possible to produce structure-contour maps for any one seam or several seams, showing minor folds, domes, or basins superimposed on the general dips or regional structures of the coal measures as a whole. A limited amount of this work has been carried out in some of the English and American coalfields, and it was commenced in Germany before the war, while in Australia it has been pioneered by E. A. Rudd (Geologist, Broken Hill Prop. Co. Ltd.) in the New South Wales coalfields. Rudd's work—prominent in this field—and its advantageous application in modern coal mining, were dealt with in an address delivered to colliery proprietors in the southern coalfield (Rudd, 1946). The detail structure-contour maps are of considerable value in planning colliery development well ahead of the actual working face, as is essential in modern mechanized mining. In the case of the New South Wales coalfields, Rudd's work has shown that features such as thickness of seam and ash content may vary with structure. In some seams thickness and ash content both increase towards the synclines and decrease on the anticlines, indicating contemporary folding with deposition of coal-forming débris. This result, which does not appear to have been established in overseas coalfields, provides valuable information from which seam conditions and coal qualities may be predicted, in addition to dips and grades, and used in planning development.

Another field of geological research likely to become important in the coal industry is the study of causes of rank-variation from the viewpoint of metamorphic environment. Little has yet been accomplished, but preliminary results have attracted attention in some of the British and German coalfields. In areas where analyses of coal are available from a number of points, "iso-vols" or "iso-carbs" (representing lines of equal rank) are plotted on a map. In almost all coalfields areas treated in this way exhibit some orderly trends in rank-variation, either about a centre or across the area. Having obtained the rank-variation map, the geologist is able to investigate causes of rank change. It may be due to unequal loading with superimposed strata associated with differential sinking during deposition, or subsequently. It may also be due to heat from intrusive igneous bodies, or to unequal distribution of pressure and heat developed by lateral forces and local folding of the measures, or even to topographical relief existing on a surface uplifted and eroded soon after deposition but removed later by peneplanation. If the cause of rank change can be determined for a particular coalfield, it is then possible to predict rank-variation beyond the limits of the area in which it is known, by studying the regional behaviour of the responsible factor. It is believed that results of this nature will throw new light on processes of coalification, and provide important data for estimation of reserves of different kinds of coal and for planning future coalfield development. The results of ultimate and proximate analyses, for representative seam samples, have been used as a basis for rank-variation. This is not entirely satisfactory, as lateral changes in proportions of banded constituents in the coal may introduce errors greater than variations due to rank differences. It is felt that greater accuracy is required, and that analyses of pure vitrain separated from the coal should be used, or possibly a more precise means of measuring rank such as some physical or optical property of the vitrain.

Observations have been made, and investigations carried out, for many years in connection with the behaviour of coal measure strata during subsidence from mining operations in both America and England. Specialized research on strata control is now being carried out by the Safety in Mines Research Board at Sheffield, in England (Phillips, 1946). This has introduced another new field of geological work in which the study of advanced tectonics is being applied to problems regarding distribution of forces, and stability of strata, associated with coal mining operations. The properties of different rock types are being studied with respect to critical forces in breaking, shearing and bending, and investiga-

tions are being made of distribution of pressure forces in roof, walls and floor sediments of mine workings, and also concentrations of pressure in underlying and overlying beds, with the object of determining maximum size and nature of safe excavations for the particular rocks with which any seam is associated. It has been established that mine workings may be disturbed, and dangerous falls of rock caused, by local concentrations of pressure due to mining operations in seams at higher levels. Results of this work are likely to prove very important in planning new mining operations with greater safety, and general economy of production, particularly where several seams are to be worked at different levels in the same locality.

Stratigraphical Correlation.

Closely associated with field geology is the application of micro-palaeobotany to problems of stratigraphical correlation of coal seams, where continuous outcrops cannot be mapped and where horizons with typical macro-fossils, or distinctive lithological features, are absent. The study of microspores has been used successfully in some cases, and promising results are being obtained, although the method is not yet fully established. Limited vertical ranges or the presence and absence of specific microspore types in different sections of a coal measure series has so far proved the most reliable in correlation.

The use of characteristic assemblages was originally believed to be the most logical and satisfactory method, as the assemblage was considered to represent the plant community which contributed to the coal-forming debris of a particular seam. Recent work, however, has shown that different coal types, particularly bright and dull varieties, contain different assemblages at the same place in a seam. This is an important factor as the normal method of sampling, involving a vertical channel sample across the seam may introduce errors owing to variations in relative proportions of "brights" and "dulls" from place to place. Very little work has yet been done on the persistence of assemblages in the bright and dull sections of coal seams, and there does not appear to be any general agreement as to whether the two coal types should be sampled separately or not in studying seam assemblages. The reason for different assemblages in bright and dull coals is somewhat obscure, but it may be related to differences in conditions of accumulation producing the two coal types. The dull coals, containing a high proportion of subaqueous, swamp vegetation, are believed to represent peat formed beneath a covering of shallow water, whilst the bright coals derived largely from coarse woody material, probably originated from a peat bed the surface of which stood slightly above water-level. These conditions would certainly favour different types of vegetation, resulting in the preservation of different microspore assemblages in each case.

Classification.

Many different systems have been devised for the classification of coals, based on chemical and physical properties, palaeobotanical features, geology of occurrence and economic uses. Some have found application in restricted fields of research or utilization but none has proved satisfactory for universal adoption by all concerned with coal, in all countries of the world. An excellent review of coal classification has recently been made by R. A. Mott (1948) of the Midlands Coke Research Association, in England.

Coals vary in several different ways over a very wide range, and no one coalfield contains coals representing all variations. People with different interests look upon coal variation from entirely different viewpoints, and in the majority of cases classifications have been based on a limited range of variation found within one coalfield, or a group of coalfields, in one country. They have

usually been devised to meet the requirements of a restricted field of interest rather than all purposes for which coal classification is required. Some of the individual systems have approached the necessary requirements for universal adoption, but they have not really provided a common language in which the geologist, chemist, coal miner and coal user can reach an understanding. As a result of this situation a general and rather vague classification appears to have evolved somewhat of its own accord, embodying certain desirable features of many different schemes. It is best described as classification by rank, type and grade, and its underlying principles are becoming understood and used in all fields of interest in all countries. This classification takes into consideration the three independent variable factors responsible for all kinds of coal and their different uses. The rank of a particular coal is the stage it has reached in the natural process of coalification. It is commonly described in terms such as brown coal, bituminous coal or anthracite, while intermediate or special stages are referred to in terms such as low-rank bituminous, coking bituminous or semi-anthracite. Foreign countries employ terms with equivalent meanings, such as the German usage of braunkohle, steinkohle and anthrazite for major rank subdivisions, and flammkohle, fettkohle and magerkohle for the intermediate or special stages referred to above. Type variation is related to the nature of the original organic débris from which the coal was formed. Types commonly recognized include the bright and dull varieties of normal humic coals, the cannel coals, and the torbanites or boghead coals. Of these the normal humic coals are derived mainly from coarse remains of wood, bark and leaves accumulated and preserved under conditions which produce bright coals containing an excess of vitrain and clarain, or produce dull coals consisting mainly of durain. The cannel coals are derived from finely divided plant remains with spores and resin, while the torbanite or boghead types are produced essentially from algal débris. Each coal type exhibits rank variation throughout its particular metamorphic series. The third variable factor is grade, influencing the usefulness or quality of any coal type of any rank. It depends on the amount of mineral matter introduced during deposition, and the coal is usually described simply as high, medium or low grade, with respect to its ash content.

The terminology of this general system of classification has not been specifically defined, but all coals can be described by using three terms, referring to rank, type and grade, all of which may vary independently. A statement such as "bright, high-grade, coking-bituminous coal" is clearly understood by all concerned with coal, and at the same time has a definite scientific meaning. For more exact designation the user of coal may specify grade in terms of ash percentage, or use B.T.U. values and size grading; the chemist or geologist may refer to rank in terms of percentage of volatile matter or carbon; the palæobotanist may describe a particular type by using generic names of predominating plants, but the same general underlying system of classification prevails. There is much room for refinement of the system and standardization of terminology, but its clarity and simplicity must be maintained, otherwise it will not be universally understood and used, and will immediately lose its value as a classification.

The most useful research in coal classification would seem to be further clarification and improvement of the general system already adopted in principle, rather than attempting to formulate new and novel schemes with strange terminology and limited application. Furthermore, it appears most important that research should be designed to make a contribution to coal classification, rather than the classification of coal in a certain country or coalfield.

Petrology, Coalification and Fundamental Nature of Coal.

Research of this kind is of a purely fundamental nature, but results usually find direct or indirect application in some practical field almost as soon as they have been established. Facilities, however, for true fundamental research on coal are relatively limited in all parts of the world, apparently because the research worker cannot always be certain of the nature of data he is likely to produce, and also because the true value of his results, in the field of practical problems, is difficult to appreciate until after they have found application.

Work in coal petrology has made good progress in recent years. Early work led to an understanding of relations between the macro- and micro-constitution of coal, and more recent work has placed coal petrology on a firm and quantitative basis. Once a clear conception of the micro-constitution of coal (recently reviewed; Dulhunty, 1946) was established, detail studies were possible of the specific nature of the macerals and banded constituents, and their relations to properties of different coal types. This is leading to a clearer understanding of how coal types vary and why each behaves as it does in commercial utilization.

Research in America, initiated by Thiessen (1947) and his colleagues at the United States Bureau of Mines, has made important contributions to coal petrology. Highly efficient methods have been developed for cutting thin sections across the full thicknesses of coal seams, studying the micro-constitution of coal types, and making petrographic analyses of coal seams. It has been shown that many properties, important in utilization, can be correlated with micro-constitution and predicted from results of petrographic analyses, particularly in cases where type and structure of coal are more significant than its rank. For example, it has been established that vitrinite is far more reactive to hydrogenation than fusinite; that it is responsible for agglutinating properties during coking; and that the two constituents give different proportions of mixed organic acids on mild oxidation. Petrological work of this nature is already finding application in the evaluation of coal for industrial purposes such as coking, hydrogenation and low-temperature carbonization, and it appears highly probable that it will provide important data in connection with the use of coal for production of liquid fuels and chemicals.

In England, the work pioneered by Stopes, Wheeler and Seyler has thrown a great deal of light on the palaeobotanical structure of coal, and established a basis for the microscopical study of macerals making up the banded constituents. Seyler's more recent work on the reflectivity of coal macerals, or the amount of vertical incident light reflected from polished surfaces, has produced interesting and surprising results (Seyler, 1941). He maintains that reflectance, which increases from vitrinite to fusinite, does not vary continuously but rather by nine steps or values, and that there is a constant ratio between the reflectance values of any two successive steps. All macerals derived from plant tissue appear to conform to one of the nine values termed components in the vitrinite-fusinite series. In the early stages of coalification plant tissue would seem to undergo differentiation into macerals representing a wide range of components. As coalification proceeds beyond lignite rank, reflectance values are stepped up by metamorphism and the macerals pass from lower to higher components. This suggests some kind of fundamental mechanism governing progressive changes from slightly altered plant material to the highly complex substances in bituminous coals, and may indicate the existence of a series of specific chemical structures, or physical conditions, representing steps in the polymerization processes associated with coalification. When satisfactorily established and interpreted, Seyler's results promise to provide new and extremely valuable techniques for quantitative determination of rank in coal, and for the study of

chemical and physical properties dependent upon rank variation. Nothing, however, has yet been established regarding the significance of his discovery, and the apparent absence of any step-wise variation in all known chemical and physical properties of coals has caused a certain degree of reluctance in accepting his findings. Further investigations, and verification, of discontinuous variation in reflectance and other properties is urgently needed, and will probably constitute an important field of petrological research in the future.

The more botanical aspects of coalification are being studied actively by Schopf (1947), Cady (1942) and others in the United States. Their work is gradually leading to a clearer picture of the preservation of various kinds of plant material, and the way in which they are changed into coal substances of lignic and cellulosic origin. It is also providing information regarding relative rates of change in coalification of specific plant substances such as spores, cuticle, normal woody tissue and products of humic degradation, and it emphasizes the existence of the two distinct processes of *vitrinization* and *fusinization*. It is generally agreed that both processes commence early in the history of coalification, and that woody material may follow either process of change without respect to its original type or nature, but the cause of differentiation still remains obscure. Most workers now maintain that fusain is a product of a process initiated soon after burial, but some still believe that it may possibly represent charcoal from ancient forest fires. The remarkable resemblance of fusain to normal charcoal, and its presence in some brown coals, appears to be responsible for theories claiming all fusain to be charred wood.

Recent observations made in peat and brown coal deposits in Australia, England and Germany strongly suggest that practically all fusain is formed by coalification after deposition and preliminary compression. In deposits of advanced brown coal rank, it normally takes the shape of pieces of wood compressed parallel to the bedding plane, and some fragments consisting partly of fusain and partly of vitrain exhibit the same amount of compression throughout. This would seem to indicate fusinization after burial, as hard brittle charcoal would be crushed or else retain its original irregular shape if strong enough to withstand pressure. In some immature deposits, however, where cover is small and the brown coal is so soft that pressure from overburden is of a hydrostatic nature rather than a vertical compressional force, occasional pieces of fusinized wood showing very little flattening are present, but such immature deposits seldom contain the proportion of fusain found in higher rank coals. In view of this, and the possibility of introduction of charcoal into peat deposits, it is felt that a small amount of the fusain in coal may represent wood charred before burial, but most of it almost certainly originated as a product of fusinization after deposition. It is highly probable that future research on chemical, physical and optical properties of constituents in low rank coals will provide a means of distinguishing between fossil charcoal and fusain formed after burial. Such results would elucidate the long-disputed origin of fusain, and make a valuable contribution to the study of coal constituents.

The most important progress in research on the fundamental nature of coal substance, during recent years, has been made in the field of physical chemistry and the work is becoming known as "coal physics". The investigations (recently reviewed in detail—Dulhunty, 1946) were carried out mainly in England, and included the study of X-ray diffraction, rheological properties, sorption properties and surface chemistry, magnetic and electrical properties, and optical properties. Results have provided valuable information regarding the aggregational state of coal substance between microscopical and molecular dimensions, establishing coal as a highly polymerized substance in the form of an isogel with definite micellar structure. Some indication has also been obtained of molecular structures and packing within the micelles, and the study of coals

varying widely in rank has given a reasonably clear picture of the evolution of the micellar structure during coalification. Also, it has been shown that many properties of economic importance depend largely on the physical condition of coal, as well as its chemical constitution. Research of this nature is essentially fundamental and progress is slow, although its importance is gradually becoming recognized and it is likely to take a prominent place in future investigations.

Chemical research on the nature of coal, and its metamorphic evolution, has made relatively little progress owing to difficulties encountered in studying its molecular structure without first subjecting it to processes of oxidation or thermal decomposition which produce substances bearing very little relation to the original coal molecule. The most useful information has been obtained by mild oxidation, partial hydrogenation and solvent extraction of different petrological constituents in coals of various ranks. Little conclusive evidence has been produced, but results generally indicate an increasing degree of aromatization in higher rank coals and in more fusinized constituents, associated with elimination of oxygen and hydrogen from the more aliphatic structures believed to be present in the humic degradation products of plant material. Progress in coal physics, however, has opened up a new field of attack for the chemist, and it is almost certain that the application of advanced techniques in physics and organic chemistry will, before long, provide a wealth of new knowledge about coal, so urgently needed for its more economical use as a fuel and as a raw material in the chemical industry, and for the solution of other problems in fundamental research.

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A GENS OF DALMANITID TRILOBITES.

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(Communicated by DR. IDA BROWN.)

With Plates I-II.

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INTRODUCTION.

In the Palæozoic rocks of eastern Australia there is a closely related group or gens of genera and species of trilobites which has heretofore been covered by the single name *Dalmanites meridianus* Etheridge and Mitchell, 1896. The present study shows that this omnibus name has covered forms belonging to the genera *Dalmanites* and *Odontochile*. The group of species concerned includes :

Dalmanites wandongensis, sp. nov.

Odontochile meridianus (Etheridge and Mitchell).

O. loomesi (Mitchell).

O. formosa, sp. nov.

As "*Dalmanites meridianus*" has been relied upon as an index fossil, stratigraphical inaccuracies have resulted from including so wide a range of forms in one species.

In the genera *Dalmanites* and *Odontochile* there are often groups of closely related species which are difficult to differentiate. When describing the dalmanitid genera of North America, Delo (1935, p. 55) noted this feature. The biological inference is that there was a high mutation pressure in these instances, resulting in a group of closely related forms. The genera named are often prolific in numbers of individuals, and this would help in the preservation of a series of forms.

GENERA OF THE GENS.

Dalmanites Barrande, 1852, genotype *Trilobus caudatus* Brünnich, 1781 (see Delo, 1935b), groups together typical dalmanitids having an elongate, non-denticulate hypostoma, genal spines, and 11 to 16 pygorachial segments. The genus is restricted to the Silurian in Europe, but continues up into the Lower Devonian in North America. In Australia the range of *Dalmanites* is probably limited to the Silurian, but this cannot be determined with certainty as yet, as there are many unsolved stratigraphical problems relating to the boundary between the Silurian and the Devonian.

The diagnosis of this genus is unusual in that it relies on the hypostoma, which is preserved comparatively rarely, and very seldom *in situ*. It needs to be *in situ* if it is to be actually proved that it belongs to a particular species. The hypostoma is also a "conservative" part of the exoskeleton, varying little from species to species, and sometimes even from genus to genus. The diagnosis

of *Dalmanites* is unusual, too, in that it cites no features of the dorsal side of the cephalon, whose morphology provides the chief *fundamenta divisionis* of families, genera and species in the Trilobita. Furthermore, the diagnosis depends on features of the pygidium, which also is generally a conservative part of the exoskeleton, i.e. its variations are usually so small and few that they do not assume taxonomic significance of generic rank. The biological inference from these facts is that while the trilobites of the Dalmanitidæ maintained the general dalmanitid impress, mutations took place in conservative parts of the exoskeleton, viz. the hypostoma and the pygidium. The diagnosis thus selects features which are taxonomically significant but not necessarily biologically important.

Odontochile Hawle and Corda, 1847, genotype *Asaphus hausmanni* Brongniart, varies from *Dalmanites* in having a denticulate hypostoma, and 16 to 22 pygo-rachial segments. Delo (1940, p. 55) found also that the larger size of *Odontochile* is a helpful guide. *Dalmanites* and *Odontochile* merge into one another, as is illustrated in the gens of *Dalmanites meridianus*. *Odontochile* arose out of *Dalmanites* and is limited to the Lower Devonian. The obvious close relationship of the Australian gens of dalmanitid trilobites now described makes it almost certain that in this case *Odontochile* arose in the Australian area from an Australian *Dalmanites*, and so independent of its genesis in other areas. *Odontochile* may thus consist of groups which have arisen in various parts of the world, and which are closely homologous and isochronous, but actually independent mutations or series of mutations. Evidence is accumulating in support of such a view for a number of fossils. Or to express it another way, because *Odontochile* is found in Australia and North America, it does not necessarily mean that the form originated in one area and migrated to the other. There are records of new mutations in living forms where the same mutation has arisen in different parts of the world at the same time. It would appear that genes have a tendency to alter their constitution in one direction rather than in others, and thus the same mutation may take place in what are apparently the same genes though in different parts of the world. If this is so, then mutations depend on some inherent structural factor as well as perhaps on some external influence (for instance, the influence of X rays on the mutation rate).

R. and E. Richter (1931) have pointed out how *Dalmanitina*, *Dalmanites* and *Odontochile* form a phylogenetic sequence.

The diagnostic features are unusual in *Odontochile* as they are in *Dalmanites*. In a mobile animal the anterior end is naturally more specialized, as it is nearest the sources of stimuli which guide its movements. The great amount of specialization in the anterior end (cephalization) readily provides a basis for classification, and that is why from the Arthropoda to the Mammalia cephalic structures possess both biological significance and taxonomic usefulness. The diagnoses of *Dalmanites* and *Odontochile* provide an exception to this general rule. Probably the addition of extra segments in the pygidium of *Odontochile* was not a development of much biological moment. It appears to be part of the general enlargement of the animal, and the advantages (as far as we can see) simply those of larger size and weight. The denticulate hypostoma of *Odontochile* probably gave more area for muscle attachment, and new angles of muscle action. However, the superseding of *Dalmanites* by *Odontochile* must surely mean that the new structures were of some biological advantage. But we are limited by not being able to discover what changes there were in the soft parts of the animals concerned.

SOME SPECIES OF THE GENUS.

Dalmanites wandongensis sp. nov.

Plate 1, figs. 1-4.

Phacops (Odontochile) caudatus McCoy, 1876, pp. 13-15, Pl. XXII, figs. 1-7; Pl. XXIII, figs. 7, 8, 9-10.**Type Material.**

Holotype, consisting of the internal cast (steinkern) of a pygidium in bluish-grey, very fine-grained sandstone from "Wandong, near Kilmore", i.e. the Geological Survey of Victoria fossil locality Bb 18 on Broadhurst's Creek. The specimen was presented to the University of Melbourne Dept. of Geology by Mr. F. H. McK. Grant on 24.6.31, and is now Reg. No. 1946 in that department.

Two paratypes, consisting of counterparts of an almost complete cephalon inferred to belong to the same species, preserved in mottled greyish very fine-grained sandstone from "Wandong, Victoria", probably the same locality as the holotype. The specimens are Reg. Nos. 420A and 420B of the Department of Geology Museum, University of Melbourne. The counterparts are an internal cast or steinkern, and an external mould.

Description of Holotype.

About 27 mm. wide at anterior end, and 25 mm. long without terminal point, i.e. as actually preserved. The rachis is 6 mm. wide anteriorly, and 2 mm. wide posteriorly just before it is rounded off. There are ten pleural segments, the elevated portion of each being divided throughout its length by a median furrow. The anterior ribs are slightly deflected backwards, and this deflection is strongly increased about two-thirds of the distance to the margin. The amount of general deflection increases with each rib until the most posterior one is almost parallel with the median longitudinal axis of the pygidium.

Fourteen pygorachial segments can be counted. They are flattened and rounded at their ends in the anterior part of the pygidium where the segments are fully developed. The margin is entire. The perimeter of the pygidium describes a more or less equilateral triangle. The terminal spine is incomplete, but its morphology can be seen in McCoy's Plate XXIII, figs. 9-10. On the right side of the pygidium the doublure is shown; it is 2 mm. wide.

Description of Paratypes.

Cephalon sub-triangular in outline, the margin tending to form a point in front of the glabella. Cephalon tumid, rising about half a centimetre above the plane of the margin. Width 4 cm. and length 2 cm. The glabella is tumid but the eyes rise even higher than it. The axial furrows, if produced as far as the longitudinal median axis of the trilobite, make an angle of about 22° . The first (most anterior) pair of glabellar furrows are oblique, and make an angle of about 70° with the median longitudinal axis. The second and third pairs of furrows are transverse, narrow, and deep; neither reach the axial furrows. The neck furrow reaches the axial furrow, but the third and second glabellar furrows respectively have their outer ends progressively further away from the axial furrows.

The posterior margin of the cephalon makes an angle of about 60° with its lateral margin. The general spines are wide, and probably long (judging by the convergence observed on the part preserved, and McCoy's Plate XXIII, fig. 7).

The eyes are large and very elevated (Pl. 1, figs. 3-4). Anteriorly, they reach the end of the first glabellar furrow, and posteriorly they almost reach the neck furrow. The visual area is almost vertical, being directed slightly upwards and outwards. The visual area measures half a centimetre high by $1\frac{1}{4}$ cm. wide.

There are about 486 lenses in the eye, made up of 27 rows in the middle with 12 lenses each, and on each side of that, 10 rows with numbers gradually descending from 11 to 4 lenses per row. Thus there are 47 rows of lenses present. This description is made from the right eye, which is the better preserved, and which is present also in the counterpart. The external mould of the eye shows that the lenses were most strongly convex on their outer surfaces, while the internal cast shows that on their inner surfaces the lenses were also convex, though not so strongly. Each lens must therefore have been quite bulbous, and possessed of at least some of the properties of a "bull's eye" lens.

The external mould shows that the surface of the cephalon possessed a fine granular type of "ornament".

Comment.

McCoy (Pl. XXII, fig. 3) figured a hypostome which is non-denticulate, thus providing further evidence that the genus is *Dalmanites*. The specimens figured by McCoy were housed in the National Museum, Melbourne, but some of them cannot now be located, including the cephalon (Pl. XXII, fig. 1). The number of segments cannot be counted on the pygidia available, except the specimen figured in Pl. XXII, fig. 6, but this is exceptionally wide and may well be a variant of the species as *O. loomesi* is of *O. meridianus*. All McCoy's specimens come from the same locality as the holotype.

Odontochile meridianus (Etheridge and Mitchell.)

Hausmannia meridianus Etheridge and Mitchell, 1896, pp. 504-509, Plate XXXVIII, figs. 1-8; Plate XL, fig. 1.

Dalmanites meridianus Mitchell, 1919, pp. 443-446, Plate XV, figs. 3-4; Plate XVI, figs. 6-7.

Type Specimens.

Etheridge and Mitchell did not name a holotype when they described their species in 1896, but in 1919, when Mitchell was describing the closely allied *O. loomesi*, he included in his plate XV a photograph (a drawing was published with the original description) of a complete specimen which he referred to as "the original type specimen of *Hausmannia meridianus*". It is the obvious choice, and so this specimen may be regarded as the holotype and the other specimens figured in the original paper as paratypes. Mitchell figured three more pygidia belonging to *O. meridianus* in his 1919 paper (Pl. XV, fig. 4, and Pl. XVI, figs. 6, 7) and these may be regarded as hypotypes.

Generic Position.

Originally described as *Hausmannia*, the above species was later referred to *Dalmanites* by Mitchell (1919), but is now referred to *Odontochile* because the holotype has 17 pygorachial segments, and the form therefore falls within this genus by definition (more than 16 pygorachial segments). A hypotype figured by Mitchell (1919, Pl. XVI, fig. 6) shows 18 pygorachial segments.

Etheridge and Mitchell (1896, Pl. XXXVIII, fig. 8) figured a damaged hypostome, to which reference was not made in the text. In size and proportions it corresponds fairly closely to hypostomes of species of *Odontochile* in Victoria, but no denticles (such as are characteristic of that genus) can be seen in Etheridge and Mitchell's drawing.

***Odontochile loomesi* (Mitchell).**

Pl. 1, figs. 5-6.

Dalmanites (*Hausmannia*) *loomesi* Mitchell, 1919, pp. 441-449, Plate XV, figs. 1-2 ; Plate XVI, figs. 3-5.

Type Specimens.

Mitchell did not name any types and so all his figured specimens must be regarded as syntypes. The first specimen figured (Pl. XV, fig. 1) is a complete carapace, and the description is largely based on it. This therefore is selected as a holotype and becomes the lectoholotype. The other specimens figured are lectoparatypes. Through the courtesy of Mr. H. O. Fletcher, palæontologist, Australian Museum, Sydney, I have been able to examine the lectoholotype, and rephotograph it (Pl. I, figs. 5-6).

Generic Position.

This species is referred to *Odontochile* because the lectoholotype possesses 16 pygorachial segments, and the lectoparatypes possess about 20 and 16 respectively. Describing the pygidium, Mitchell says: "Axis consists of 16 to 20 rings (dependent on the state of maturity)." The form therefore belongs to *Odontochile* by definition. In discussing pygidial segmentation, Mitchell (p. 445) mentions that Silurian forms do not have more than 16 segments, then states that his species has up to 20, but claims nevertheless that his species "shows transition towards the pygidial segmentation of the Devonian species". He seems to have thought that Reed's (1905) definition of 12 to 16 segments for Silurian species referred to the number of pygopleural segments, whereas it refers to the number of pygorachial segments.

***Odontochile formosa* sp. nov.**

Plate II, figs. 1-2.

Type Material.

A cast of a complete carapace constitutes the holotype (Univ. of Melbourne, Dept. of Geol., Reg. No. 882, presented by Mr. W. McCormack). It is preserved in bluish grey, very fine grained sandstone, which is very compact, so much so that the original calcareous material is preserved in some of the fossils, which is unusual in the Silurian and Devonian rocks of Victoria.

Locality.

The holotype was collected from a Country Roads Board quarry, 1½ miles 20° W. of S. from Kinglake West (Tommy's Hut) Post Office. It is near the headquarters of Scrubby Creek, and the military map reference is Kinglake sheet 247,847.

Etymology.

The trivial name is derived from the Latin *formosus*, "beautiful in form", a reference to the elegant proportions and well-developed structures of the species.

Whole Carapace.

The carapace is large, being about 16 cm. long and 9 cm. wide. The general outline is ovoid. Cephalon with large eyes and very long genal spines. Pygidium large and mucronate. Whole carapace covered with fine granulation. The carapace has been compressed dorso-ventrally, the greatest displacement taking place in the cephalon.

Cephalon.

Sub-triangular in outline. A flat border 3 to 4 mm. wide is shown on the left side of the cephalon, but as the frontal margin is not preserved, it cannot be proved whether this border extended right round the cephalon or not. As preserved, the cephalon is 3.2 cm. long and 9 cm. wide, a ratio of length to width of about 1:2.8.

The glabella is approximately 3.8 cm. wide anteriorly and 2 cm. wide posteriorly. There is a central longitudinal furrow in the frontal lobe, believed to be due to compression of a tumid carapace. The axial furrows, if produced as far as the median longitudinal axis of the trilobite, make an angle of about 50°. The first (most anterior) glabellar furrows make an angle of about 140°. The second and third furrows are more or less transverse, and reach the axial furrows. The free cheeks are moderately tumid for this genus. The marginal furrow and neck furrow make an angle of about 50° (left side of cephalon measured).

The eyes are large, reaching from the first furrow to the third. A line joining the ends of the left eye measures 1.5 cm. The facets are small, circular and closely packed, there being 12 or more (the preservation is not good) in the central rows, and less towards the ends. There are of the order of 40 rows.

The genal spines are long and strong. On the right side of the holotype an almost complete genal spine is preserved, but it is turned under somewhat by compression. As preserved, it measures about a centimetre wide where it leaves the cephalon proper, and reaches as far as the eighth segment of the thorax, where it is broken off, the width there being 2 mm.

Thorax.

The thorax consists of eleven segments, and is approximately 6 cm. long and 9 cm. wide, a ratio of 1:1.5. The greatest width of the axis is 2.5 cm., a ratio of axis to thorax of 1:3.6, and of axis to pleuron of 1:1.3. Each pleuron is divided by a narrow median furrow for practically its whole length. The outer ends of the pleura are deflected ventrally, and terminate in pleural spines.

Pygidium.

The pygidium has 18 pygorachial segments plus the rounded terminus. There are 12 pygopleural segments. The right half of the pygidium is partially obscured by the matrix, but judging by the left half the pygidium must be 9 cm. wide. The length (without the terminal spine) is about 6.5 cm., a ratio of width to length of 1:1.4. The mucro is broken, but was 1 cm. wide where it joined the rest of the pygidium. It appears to be narrowing rapidly.

The greatest width of the rachis is 1.7 cm. (i.e. about one-fifth of the width of the pygidium), and the smallest 0.5 cm. The rachis tapers gradually and ends before reaching the terminal spine. The posterior margins of the pygorachial segments nearer the thorax arch in the middle in an anterior direction. Like the thoracic axial segments, the anterior pygorachial segments have short furrows towards their ends. The posterior pygorachial segments become mere rings without specialized structure.

The anterior pygopleural segments are gently curved posteriorly. This curvature increases until the last segment is actually parallel to the longitudinal axis of the trilobite. A narrow median furrow is present in all the pygopleural segments. Each furrow commences at the rachis and terminates abruptly just before reaching the margin of the pygidium, which is fused into a continuous line. Where the pygidium is broken away a little, a well-developed doublure (of the order of $\frac{1}{2}$ cm.) can be seen.

Comparison.

The new species simulates closely *Odontochile dunbari* Delo from the Devonian of Missouri (Bailey limestone). *O. dunbari* has the same number of both pygorachial and pygopleural segments as *O. formosa*; it has a similar deflection of the pygopleural segments, and a similar furrowing; the pygorachial segments have a similar arching of the posterior edge; and finally, the two species are of similar proportions. The cephalon and thorax of *O. dunbari* are unknown (see Delo, 1940, p. 56).

DETERMINATION OF DALMANITIDS.

In members of the Dalmanitidæ, the number of pygorachial segments is important both for generic and specific determinations. But the number of segments that can be counted varies with the maturity of the animal, and so it is very important to have a mature specimen on which to base a determination. Delo has pointed out that size is a helpful guide in making generic determinations, and it is also a specific character. Here again there is variation with stage of growth. It is therefore important in determining any of these forms to be sure that the trilobite is a mature specimen, otherwise the determination can be misleading. It is desirable to have a range of specimens in hand before a new species is described, and there is uncertainty, in my opinion, in describing a new species from a solitary pygidium as has been done.

The genus *Dalmanites* grades into the genus *Odontochile*, and difficulty can attach to their separation. However, most difficulties disappear if mature specimens are chosen, and then the criteria set out in the diagnoses of the genera objectively applied.

CHARACTER OF GENS.

The fact that for over 50 years so many species belonging to two genera have been given the one name indicates the solidarity of the gens. The forms are very much alike and constitute a closely related genetic sequence. The species described in this paper are apparently only some of a number belonging to the gens. Material seen from Tasmania, Victoria and New South Wales suggests the presence of other species. The gens is characterized by large eyes set high in the exoskeleton so as to rise well above the glabella. As far as it has been worked out, the genealogical relationships appear to be as follows:

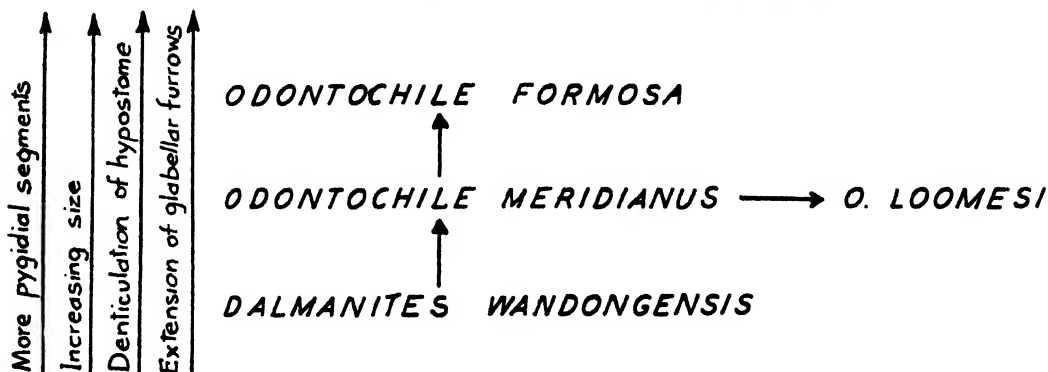


Fig. 1.

O. loomesi is very closely related to *O. meridianus*, but its different proportions from the other members of the gens shows that it is a branch away from the main line of development.

The signs of maturation in these trilobites are larger size, more advanced development of the posterior segments of the exoskeleton, greater tumidity, deeper impression of glabellar furrows, and in general a better development of the animal's exoskeletal structures. It is interesting to note that these same factors operate in the evolution of the gens. The only new structure in the sequence is the generic one of denticles on the hypostome—a minor specialization of an already existing part.

The glabellar furrows are of considerable phylogenetic significance, and their development in the gens is consequently of some interest and importance. In *D. wandongensis* the glabellar furrows do not reach the axial furrow. In the younger specimens of *O. formosa* (Pl. II, fig. 2), they reach nearer the axial furrow than they do in *D. wandongensis*, but still they do not reach it. In well-matured specimens of *O. formosa* like the holotype, however, the glabellar furrows do reach the axial furrow, although the part nearer the axial furrow is comparatively shallow. Nevertheless the glabellar furrows do definitely conjoin with the axial furrows. Thus in the life history of the individual *O. formosa*, the trend found in the gens as a whole is exemplified.

STRATIGRAPHICAL CONSIDERATIONS.

The genus *Dalmanites* was believed to be restricted to the Silurian until Delo found that in North America (though as far as is known not elsewhere in the world), there is a slight overlap into the Devonian. He has described forms from the Helderbergian. *Odontochile*, as far as is known, is restricted to the Devonian.

Odontochile formosa comes from beds which have been referred to the Lower Devonian. *Odontochile meridianus* and *O. loomesi*, on the other hand, come from beds which have been described by Dr. Ida Brown (1941) as Silurian in age. The range of *Odontochile* is therefore greater than formerly believed (as was the case with *Dalmanites*), or some revision of the age determination of the beds concerned is indicated. The beds with *Odontochile* also contain the genera *Pleurodictyum* (vide Hill, 1943, pp. 58–59) and *Dicranurus* (Gill, 1948), which are restricted to the Devonian elsewhere.

It should be noted that *Odontochile meridianus* and *O. loomesi* are not so well advanced in development as *O. formosa*, from which it may be inferred that they are older in age. A similar position was noted with *Dicranurus* (Gill, 1948).

Chapman (1914, p. 219) referred the beds on Broadhurst's Creek at Wandong to the Melbournian Series, but later (1915, p. 161, footnote) referred them to low down in the Yeringian or passage beds, making mention specifically of the presence of "*Dalmanites meridianus*". It was the presence of this fossil which influenced the reference of these beds to the Yeringian Series by the present writer in 1940 (p. 254). *Dalmanites* is a Silurian genus, but extends up into the Devonian (Helderbergian) in North America. *Dalmanites wandongensis* therefore does not determine the age of the beds at Broadhurst's Creek, Wandong. More palæontological work will have to be done before their place in the stratigraphic sequence can be established.

"*Dalmanites meridianus*" has been recorded from Killara (Gill, 1938, p. 170; 1939, p. 142). This is a species of *Odontochile*, but a determination is not attempted because the material in hand is not good enough for description. The same applies to specimens from Whittlesea (Chapman in Jutson, 1908), where the species also is an *Odontochile* (determined from F. S. Colliver Collection, No. 2784). Similarly, specimens from Tasmania (Etheridge, 1897) must await the collection of further material to effect their elucidation. The large number of pygorachial segments, a feature specially noted by Etheridge, again indicates the genus as being *Odontochile*.

ACKNOWLEDGEMENTS.

I am indebted to Mr. Harold Fletcher, palæontologist of the Australian Museum, Sydney, for information concerning New South Wales trilobite localities, and to Mr. Robert Withers, M.Sc., Dip.Ed., for similar information concerning the Kinglake trilobite. Mr. F. S. Colliver has made specimens available from his collection. Dr. Ida Brown kindly agreed to communicate this paper to the Society. The photographs were taken by Mr. L. A. Baillôt of the Melbourne Technical College, and Miss M. Johnson of the Geology Department of the University of Melbourne.

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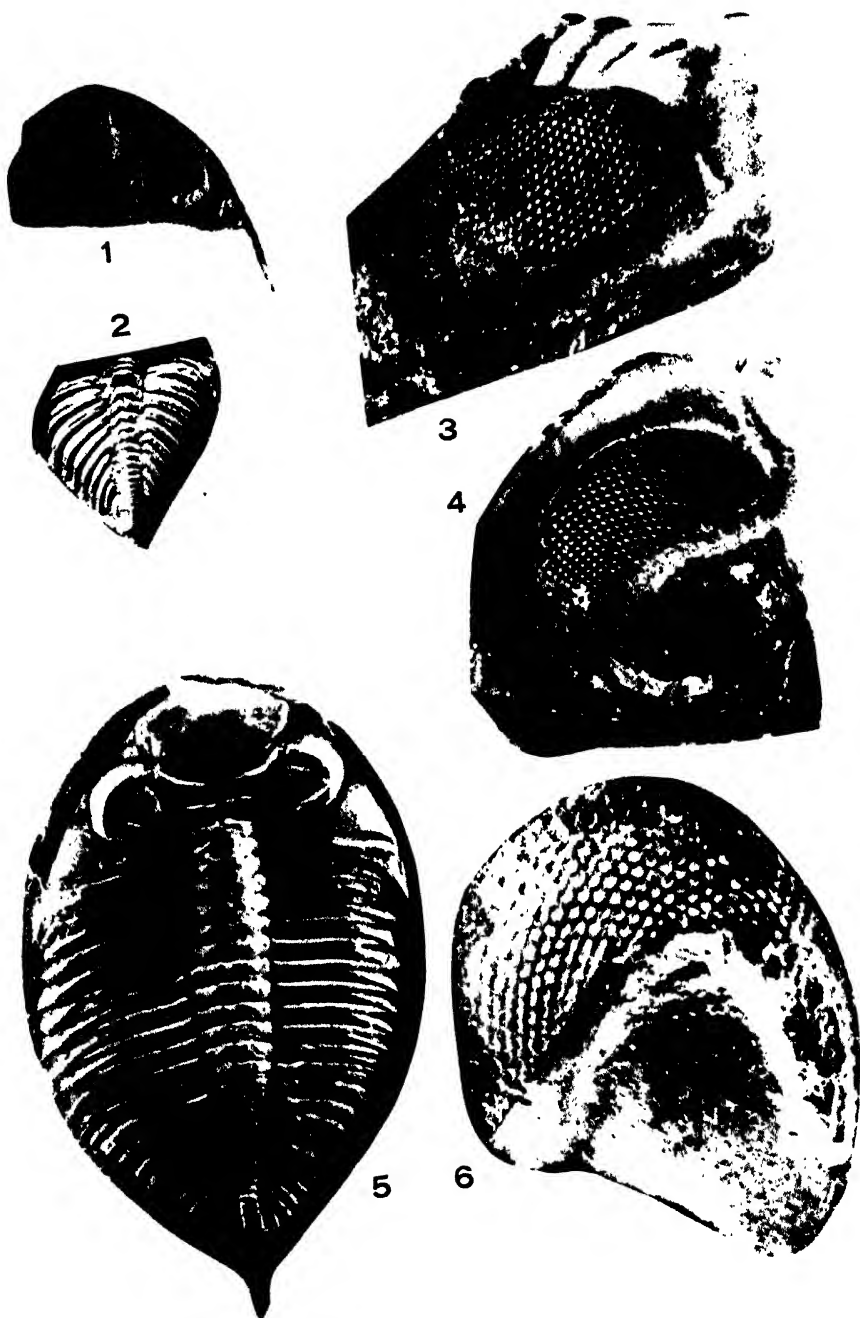
EXPLANATION OF PLATES.

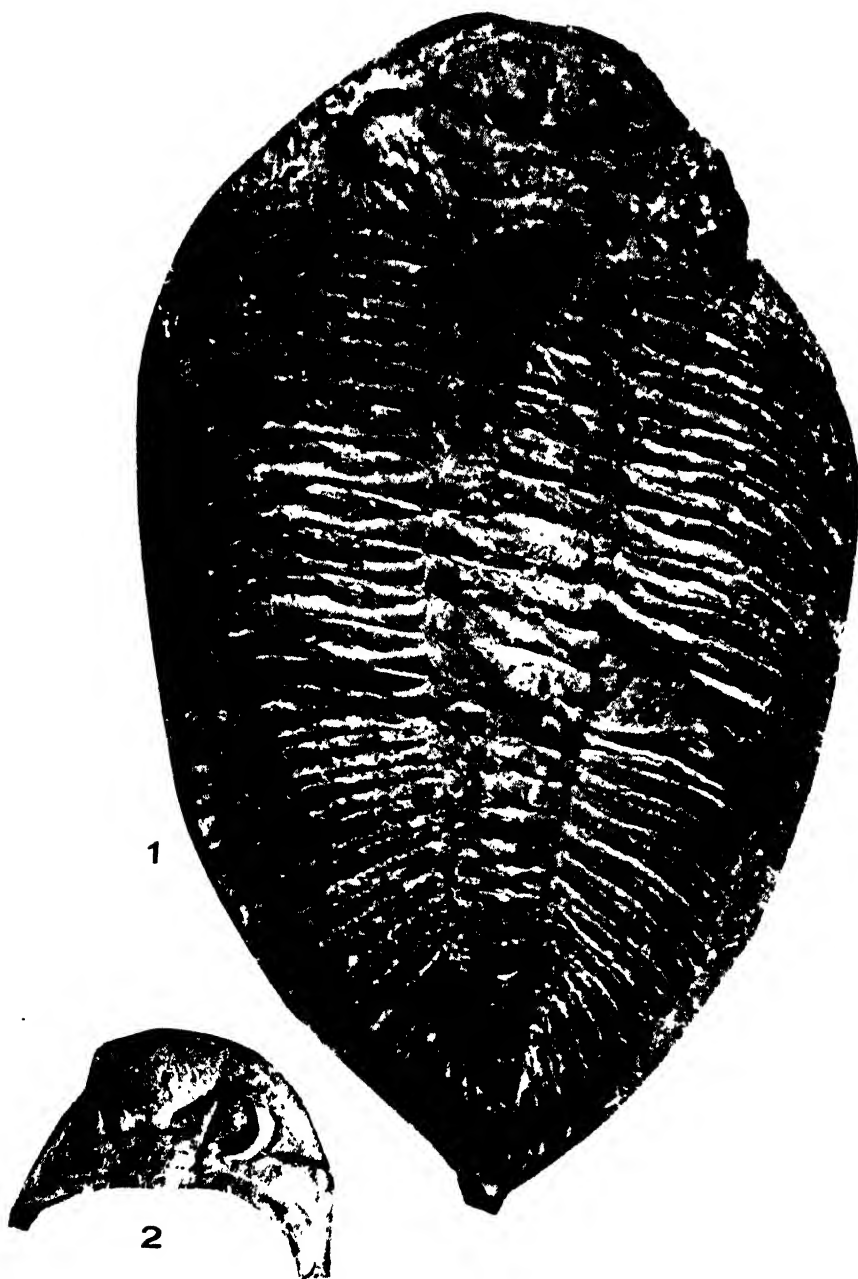
PLATE I.

- Fig. 1.—*Dalmanites wandongensis*, sp. nov., internal cast of cephalon, *paratype*. Natural size.
- Fig. 2.—*D. wandongensis*, sp. nov., internal cast of pygidium, *holotype*. Natural size.
- Fig. 3.—*D. wandongensis*, sp. nov., eye of internal cast, $\times 4$. *Paratype*.
- Fig. 4.—*D. wandongensis*, sp. nov., eye of external mould, $\times 4$. *Paratype*.
- Fig. 5.—*Odontochile loomessi* (Mitchell), internal cast of complete carapace, *lectoholotype*.
- Fig. 6.—*O. loomessi* (Mitchell), internal cast of eye, $\times 6$. *Lectoholotype*.

PLATE II.

- Fig. 1.—*Odontochile formosa*, sp. nov., internal cast of complete carapace, *holotype*. Natural size.
- Fig. 2.—*O. formosa*, sp. nov., internal cast of cephalon of young specimen from Davies' Quarry, on the western branch of Stony Creek, about a mile north of Kinglake West State School (same locality as *Dicranurus kinglakensis*), *hypotype*. Natural size. Note that the second and third glabellar furrows fail to reach the axial furrows, as they do on the mature specimen. Univ. of Melbourne, Dept. of Geology, Reg. No. 1947.





OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1947.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

Manuscript received, January 6, 1948. Read (in title only), April 7, 1948.

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times either for personal effect or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the *Nautical Almanac* for 1938 and the reduction completed by the method given there. The necessary data were taken from the *Nautical Almanac* for 1947, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

Table I gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1947). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table II gives the results of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the new zodiacal catalogue (Robertson, 1940), as recorded in the *Nautical Almanac*.

TABLE I.

Serial No.	N.Z.C. No.	Mag.	Date.	U.T.	Observer.
				h m s	
141	219	5.1	Jan. 1	12 01 57.2	W
142	631	5.6	Jan. 4	12 35 57.7	W
143	742	6.0	Feb. 1	13 38 49.3	W
144	1169	5.4	Mar. 3	10 20 16.6	R
145	1263	7.1	Mar. 31	8 50 53.7	R
147	1270	6.1	Mar. 31	10 31 04.1	R
148	1274	5.7	Mar. 31	11 52 31.9	R
149	1279	6.4	Mar. 31	12 39 20.6	R
150	1233	5.8	Apr. 27	8 24 36.2	W
151	1365	6.1	Apr. 28	8 40 57.9	R
152	1689	5.5	May 28	9 17 59.8	R
153	2330	6.3	June 30	8 56 40.9	R
154	2337	6.4	June 30	10 44 16.1	R
155	1725	7.5	July 22	9 37 25.8	W
156	2430	7.0	July 28	11 27 07.5	R
157	2605	7.1	Sept. 22	8 57 48.2	R
158	2623	7.5	Sept. 22	12 34 58.6	W
159	2781	7.4	Sept. 23	13 56 20.5	W
160	2282	5.9	Oct. 17	9 43 21.9	R
161	2852	7.4	Oct. 21	9 30 40.4	W
162	3243	7.4	Oct. 24	13 10 03.7	R
163	3062	7.5	Nov. 19	9 58 01.8	W

TABLE II.

Serial No.	Luna- tion.	p	q	p ²	pq	q ²	$\Delta\sigma$	p $\Delta\sigma$	q $\Delta\sigma$	Coefficient of	
										$\Delta\alpha$	$\Delta\delta$
141	297	+ 93	+36	87	+34	13	-0.9	-0.8	-0.3	+10.3	+0.72
142	297	+ 83	-56	69	-46	31	-0.9	-0.7	+0.5	+13.2	-0.32
143	298	+ 99	-13	98	-13	2	+0.2	+0.2	0.0	+13.7	+0.07
144	299	+ 98	-18	97	-18	3	-1.2	-1.2	+0.2	+12.9	-0.29
145	300	+100	+ 1	100	+ 1	0	-1.1	-1.1	0.0	+13.4	-0.18
147	300	+ 54	-84	29	-45	71	-0.4	-0.2	+0.3	+ 5.0	-0.93
148	300	+ 97	-24	94	-23	6	+0.4	+0.4	-0.1	+12.4	-0.43
149	300	+ 96	+28	92	+27	8	-1.1	-1.1	-0.3	+13.6	+0.08
150	301	+ 75	+66	56	+50	44	-2.0	-1.5	-1.3	+11.4	+0.53
151	301	+ 20	-98	4	-20	96	-1.2	-0.2	+1.2	- 0.9	-1.00
152	302	+ 13	-99	2	-13	98	-0.4	-0.1	+0.4	- 4.5	-0.95
153	303	+ 99	-13	98	-13	2	-0.1	-0.1	0.0	+12.9	-0.39
154	303	+ 96	+29	92	+28	8	-1.4	-1.3	-0.4	+14.0	+0.02
155	304	+ 43	-90	18	-39	82	+1.8	+0.8	-1.6	- 0.1	-1.00
156	304	+ 71	+70	51	+50	49	-1.5	-1.1	-1.0	+11.5	+0.55
157	306	+ 97	-26	93	-25	7	0.0	0.0	0.0	+12.6	-0.33
158	306	+ 98	+20	96	+20	4	+1.2	+1.2	+0.2	+13.4	+0.14
159	306	+ 95	-32	90	-30	10	-1.0	-1.0	+0.3	+13.0	-0.27
160	307	+ 99	-17	97	-17	3	-0.8	-0.8	+0.1	+12.5	-0.45
161	307	+ 25	+97	6	+24	94	-0.6	-0.2	-0.6	+ 2.0	+0.99
162	307	+ 98	-20	96	-20	4	-1.2	-1.2	+0.2	+14.2	+0.16
163	308	+ 62	+78	39	+49	61	-0.6	-0.4	-0.5	+ 5.6	+0.92

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 Robertson, W. H., 1947. *THIS JOURNAL*, 81, 34.

MICROMETRICAL MEASURES OF DOUBLE STARS.

by HARLEY WOOD, M.Sc.

Manuscript received, December 11, 1947. Read (in title only), April 7, 1948.

The following measures were made with the 11½-inch equatorial telescope of Sydney Observatory. The stars were all observed with the telescope east of the pier and the hour angle was small in all cases except one recorded in the notes at the end. There are 210 measures of 71 stars. In the table columns 1, 2 and 3 give the star's name and C.P.D. number, and right ascension and declination (1900) from Innes' *Southern Double Star Catalogue*; 4, 5 and 6 respectively the date, position, angle and distance; 7 gives the magnification used, the position of the eyes parallel (.) or perpendicular (:) to the position angle of the stars and the definition on a scale in which 5 represents perfection and 0 unworkability; 8 gives the difference in magnitude and 9 the number of nights for means.

Star	R.A. h m	Dec. ° '	Date 1900+	p °	d "	M.E.D.	Δm	
β391	0 04.3	28 33	45.896	264.1	1.67	420.2	0.1	
28°4			46.642	263.2	1.71	420.3	0.0	
			46.766	265.6	1.63	420.3	0.0	
			46.435	264.3	1.67		0.0	3n
h3447	1 31.5	30 25	46.642	104.8	1.55	420.2	0.8	
30°186			46.766	108.3	1.47	420.2	1.5	
			46.704	106.6	1.51		1.2	2n
Δ5	1 36.0	56 42	45.896	204.7	10.28	420.2	0.0	
56°329			45.918	204.9	10.31	250.2	0.1	
			45.937	204.9	10.49	250.1	0.1	
			45.967	204.8	10.49	250.2	0.0	
			45.929	204.8	10.39		0.0	4n
h3494	2 15.6	35 54	45.918	300.2	1.41	420.3	0.1	1n
36°221								
h3494	(bis)		46.604	297.7	1.36	420.3	0.1	
			46.648	295.7	1.42	420.3	0.0	
			46.673	295.7	1.37	420.4	0.1	
			46.675	295.9	1.36	420.2	0.1	
			46.703	297.5	1.33	420.3	0.2	
			46.727	296.9	1.42	420.3	0.3	
			46.755	298.4	1.28	420.2	0.2	
			46.766	297.1	1.35	420.2	0.2	
			46.694	296.9	1.36		0.2	8n
Brs.1	2 39.8	25 55	45.937	191.1				
26°255			47.038	190.8	12.18	420.1	1.2	1n
Δ12	3 13.6	64 49	46.648	103.0	18.89	420.3	1.7	
64°235			46.651	103.2	19.02	300.2	2.2	
			46.650	103.1	18.96		2.0	2n

Star	R.A. h m	Dec. ° '	Date 1900+	p °	d "	M.E.D.	Δm	
$\Delta 15$.. 40°343	.. 3 36.2	40 41	46.675 46.703 46.727 46.702	327.5 327.6 327.7 327.6	7.90 7.77 7.79 8.82	420 : 2 420 : 3 420 : 3	0.8 0.6 0.8 0.7	3n
$\beta 1004$.. 34°424	.. 3 58.2	34 46	46.673 46.703 46.727 46.755 46.714	112.3 113.2 113.7 114.6 113.4	1.84 1.71 1.84 1.81 1.80	420. .4 420. .3 420. .3 420. .2	0.5 0.3 0.5 0.5 0.4	4n
h3683 .. 59°370	.. 4 38.6	59 08	46.673 46.703 46.727 46.701	89.5 90.8 89.9 90.1	1.90 1.85 2.05 1.93	420. .4 420. .3 420. .3	0.1 0.1 0.1 0.1	3n
$\Delta 23$.. 48°777	.. 6 02.2	48 27	44.163 44.168 44.166	87.3 86.6 87.0	2.27 2.05 2.16	290. .2 290. .3	0.4 0.5 0.4	2n
$\beta 755$.. 36°1001	.. 6 31.9	36 42	44.168	256.9	1.54	290. .3	0.7	1n
M1b2 .. 60°1056	.. 8 03.3	60 06	44.223 44.226 44.302 44.250	351.4 350.0 353.8 351.7	1.66 1.63 1.85 1.71	520 : 2 520 : 2 290 : 2	0.5 0.3 0.5 0.4	3n
$\beta 208$.. 22°3752	.. 8 34.8	22 19	44.215 44.226 44.278 44.240	206.7 208.0 207.5 207.4	2.14 2.09 1.98 2.07	520 : 2 520 : 2 520 : 4	1.5 0.8 1.0 1.1	3n
h4165 .. 51°1821	.. 8 58.6	51 48	44.223 44.278 44.302 44.271	108.9 110.0 108.7 109.2	1.22 1.15 1.15 1.17	520. .2 520. .3 520. .3	1.0 1.2 0.8 1.0	3n
h4188 .. 43°3450	.. 9 08.8	43 12	46.305 47.272 47.350 46.975	281.9 282.9 283.2 282.7	2.95 2.82 2.90 2.89	300. .2 420. .3 420. .2	0.3 0.3 0.1 0.2	3n
h4220 .. 48°2532	.. 9 30.2	48 34	44.193 44.346 44.260	210.4 213.4 211.9	2.27 2.17 2.22	290 : 3 520 : 3	0.2 0.8 0.5	2n
L.P127 .. 59°1638	.. 9 57.9	59 15	46.305 47.363 47.369 47.012	264.6 266.7 267.6 266.3	7.75 7.70 7.74 7.73	300. .2 420. .2 420. .2	2.5 1.8 2.2 2.2	3n
R141 .. 66°1226	.. 10 17.2	66 40	44.302	45.1	2.17	520. .3	0.7	1n
R141 (bis)		47.272 47.355 47.369 47.332	43.1 44.0 45.3 44.1	1.93 1.86 1.93 1.91	420 : 3 420 : 2 420 : 2	0.8 0.7 0.8 0.8	3n
Brs5 .. 60°2911	.. 11 20.4	61 06	44.346 44.431 44.450 44.409	203.0 202.9 201.7 202.5	2.54 2.51 2.57 2.54	520 : 3 290 : 3 520 : 2	1.5 1.5 1.5 1.5	3n

MICROMETRICAL MEASURES OF DOUBLE STARS.

29

Star	R.A. h m	Dec. ° '	Date 1900+	p °	d "	M.E.D.	Δm	
Brs6 .. 41°5379	.. 11 23·8	42 07	46·475 47·536 47·006	168·2 168·3 168·2	13·32 13·34 13·33	300 : 2 420. 1	2·0 1·2 1·6	2n
Hdl14 .. 55°4711	.. 11 50·0	55 32	46·442 46·461 46·475 46·459	181·6 181·6 182·8 182·0	3·10 3·10 2·92 3·04	300 : 1 300 : 1 300 : 4	0·1 0·1 0·2 0·1	3n
Rmk14 .. 45°5842	.. 12 08·8	45 10	46·461 46·475 46·468	246·2 246·0 246·1	3·00 3·15 3·08	300. 4 300. 4	0·8 0·4 0·6	2n
Brs8 .. 57°5451	.. 12 19·4	57 34	43·420 43·458 43·477 43·452	336·0 336·4 335·7 336·0	5·31 5·35 5·41 5·36	290 : 3 290 : 2 290 : 3	0·3 0·2 0·5 0·3	3n
Cor138 .. 33°3255	.. 12 22·0	33 35	44·403 44·431 44·494 44·443	7·0 7·1 6·9 7·0	4·64 4·52 4·45 4·54	290 : 3 290 : 2 520 : 3	1·2 1·5 2·0 1·6	3n
R207 .. 67°2064	.. 12 40·2	67 33	44·450 44·494 44·472	9·3 8·9 9·1	1·44 1·44 1·44	520 : 2 520 : 3	0·1 0·2 0·2	2n
Cor141 .. 56°5434	.. 12 41·7	56 54	46·499 46·505 46·510 46·505	146·2 144·6 143·8 144·9	4·42 4·30 4·22 4·31	300 : 3 300 : 2 300 : 3	1·0 1·4 1·2 1·2	3n
Rmk16 .. 64°2183	.. 13 01·7	64 46	46·461 46·475 46·499 46·478	186·4 187·3 186·6 186·8	5·54 5·54 5·50 5·53	300 : 2 300 : 3 300 : 2	1·7 0·8 1·2 1·2	3n
Hrg86 .. 61°3777	.. 13 25·8	61 50	46·510 47·580 47·045	240·6 238·3 239·4	1·86 1·74 1·80	420. 3 420 : 2	0·3 0·2 0·2	2n
HIII 101 32°3512	.. 13 46·1	32 30	44·508 44·518 44·513	107·1 106·2 106·6	8·06 8·10 8·08	290. 2 290. 3	0·7 1·5 1·1	2n
β343 .. 30°3752	.. 13 46·3	31 07	44·431	265·3	0·99	520. 2	0·4	1n
Δ151 .. 55°5793+4	.. 13 50·7	55 33	43·477 43·497 43·487	45·2 44·8 45·0	23·29 23·13 23·21	290. 2 290 : 2	2·0 2·5 2·2	2n
Slr19 .. 49°6679	.. 14 01·2	49 24	44·450 44·494 44·518 44·487	282·2 283·2 285·4 283·6	1·42 1·30 1·44 1·39	520. 3 520. 3 520. 3	0·1 -0·1 0·1 0·0	3n
Slr19 .. (bis)			46·461 46·475 46·468	282·2 284·4 283·3	1·65 1·59 1·62	420. 2 420. 2	0·0 0·1 0·0	2n
h4687 .. 36°6477	.. 14 29·5	36 07	45·565 46·587 46·076	98·5 104·0 101·2	1·58 1·39 1·48	290. 2 420. 4	0·1 0·1 0·1	2n

Star	R.A. h m	Dec. ° '	Date 1900+	p °	d "	M.E.D.	Δm	
α Cen 14 32.8	60 25	42.494 42.513 42.504	0.8 1.6 1.2	7.27 7.27 7.27	290 : 2 290 : 3	0.5 0.5 0.5	2n
Δ 166 .. 64°2977	.. 14 34.4	64 32	42.499 43.477 42.988	231.9 231.9 231.9	16.00 15.72 15.86	290. .2 290. .2	4.0 4.0 4.0	2n
h4707 .. 65°2914	.. 14 45.8	66 00	44.494 44.540 44.518	51.7 50.4 51.0	0.94 1.08 1.01	520. .4 520. .3	0.2 0.1 0.2	2n
h4712 .. 54°6214	.. 14 48.1	55 01	45.584 46.461 46.480 46.175	228.0 228.3 228.0 228.1	7.27 7.19 7.13 7.20	290. .1 300. .3 300 : 2	0.8 0.4 0.2 0.5	3n
h4728 .. 46°7178	.. 14 58.3	46 40	42.499 43.554 43.026	73.6 77.5 75.6	1.84 1.85 1.84	290. .2 290 .2	-0.1 0.1 0.0	2n
Δ 179 .. 42°6963	.. 15 07.8	43 01	44.590	45.7	10.60	290 : 3	1.5	1n
Hwe78 .. 33°3881	.. 15 25.0	33 29	44.494	143.5	2.02	290 : 3	1.5	1n
h4788 .. 44°7483	.. 15 29.0	44 37	42.513 42.551 42.532	0.5 2.4 1.4	2.51 2.49 2.50	290 : 3 290 : 3	3.5 2.5 3.0	2n
Hwe79 .. 41°7323	.. 15 37.6	41 30	46.592 47.580 47.599 47.257	344.3 344.1 344.1 344.2	3.92 3.92 3.91 3.92	420 : 2 420 : 2 420 : 1	2.0 2.0 1.0 1.7	3n
Hld124 50°8526	.. 15 37.6	50 28	43.573 44.540 44.056	201.1 203.3 202.2	2.51 2.43 2.47	290 : 2 520 : 4	2.0 2.0 2.0	2n
Rmk20 65°3139	.. 15 38.8	65 08	45.603 45.617 45.610	149.2 148.9 149.0	2.28 2.11 2.20	290 : 2 290 : 2	0.1 0.1 0.1	2n
Cor193 .. 37°6639	.. 16 01.1	37 46	46.480 46.620 47.613 46.904	91.1 90.6 92.0 91.2	4.15 4.09 3.89 4.04	300. .3 300. .2 420. .2	0.0 0.0 0.1 0.0	3n
Cor197 .. 48°8449	.. 16 17.9	48 55	44.590	150.5	1.79	520 : 3	0.1	1n
Slr12 .. 47°7811	.. 16 32.5	47 35	46.587 47.613 47.689 47.695 47.396	169.1 168.1 168.0 168.5 168.4	1.52 1.50 1.47 1.45 1.48	420 : 3 420 : 2 420. .2 420 : 2	0.0 0.0 0.1 0.1 0.0	4n
Cor198 .. 47°7818	.. 16 33.3	47 28	43.573	97.2	2.75	290. .2	1.0	1n
Cor201 .. 49°9629	.. 16 43.0	49 52	42.551 42.581 43.554 42.899	45.2 41.2 44.8 43.7	3.32 3.05 3.10 3.16	290. .3 290 : 3 290. .2	0.1 0.1 0.2 0.1	3n

Star	R.A. h m	Dec. ° '	Date 1900+	p "	d "	M.E.D.	Δm	
Brs13 .. 46°8513	.. 17 11.5	46 32	42.590 42.595 42.592	214.7 214.5 214.6	4.84 4.75 4.80	290 : 3 290 : 4	4.0 4.0 4.0	2n
HIII 25 24°5859	.. 17 11.9	24 11	45.573 46.675 46.124	354.9 354.7 354.8	10.32 10.36 10.34	290 : 1 420 : 2	2.0 1.5 1.8	2n
h4949 .. 45°8580	.. 17 19.5	45 45	42.672 43.573 43.122	256.5 258.3 257.4	2.46 2.46 2.46	290. .2 290. .3	0.5 0.5 0.5	2n
R303 .. 54°8468	.. 17 36.9	54 06	44.590	106.6		290. .2	1.0	1n
Rmk22 55°8375	.. 17 48.9	55 22	42.595 42.628 42.612	90.9 92.9 91.9	2.54 2.79 2.66	290. .4 290. .2	0.8 1.5 1.2	2n
R306 .. 35°7563	.. 17 51.2	36 00	47.613 47.719 47.728 47.687	17.9 18.8 17.9 17.2	3.67 3.71 3.74 3.71	420 : 2 420 : 4 210 : 1	2.0 3.0 3.0 2.7	3n
h5014 .. 43°8434	.. 17 59.6	43 26	42.647 42.691 42.669	216.2 219.3 217.8	1.87 1.67 1.77	290 : 3 290. .2	0.1 0.1 0.1	2n
h5014 (bis)		46.587 47.708 47.722 47.733 47.437	214.2 215.7 215.4 214.2 214.9	1.78 1.75 1.65 1.74 1.73	420. .4 420 : 2 420 : 3 300 : 2	0.1 -0.1 -0.1 0.0 0.0	4n
h5027 .. 54°8761	... 18 05.5	54 23	45.666 45.694 45.699 45.686	138.0 138.4 139.3 138.6	15.05 14.60 14.63 14.76	290. .2 290 : 1 290 : 2	3.0 3.0 3.5 3.2	3n
h5034 .. 46°9202	.. 18 08.8	46 03	47.613 47.684 47.689 47.662	99.1 97.8 100.9 99.3	2.58 2.40 2.52 2.50	420. .2 420. .3 420. .2	0.5 0.5 0.5 0.5	3n
Mlb5 .. 66°3380	.. 18 24.1	66 21	42.653 42.675 42.664	293.4 293.0 293.2	4.83 4.64 4.74	290. .3 290. .2	3.5 3.5 3.5	2n
h5070 .. 22°7218	.. 18 45.3	22 08	45.685 47.708 47.719 47.722 47.208	51.0 52.7 51.2 51.2 51.5	9.65 9.34 9.60 9.43 9.50	290. .2 420 : 2 420. .4 420. .3	0.1 0.1 0.0 0.0 0.0	4n
h5085 .. 60°7269	.. 19 01.8	60 12	42.628 42.647 42.638	243.5 239.2 241.4	3.21 3.29 3.25	290 : 2 290. .3	3.5 3.0 3.2	2n
h5091 .. 31°5897	.. 19 02.1	31 08	45.757 47.684 47.728 47.733 47.226	208.8 210.0 210.5 209.7 209.8	9.06 8.88 8.99 8.94 8.97	290 : 1 420 : 3 210 : 1 210 : 2	3.5 1.2 0.8 1.0 1.6	4n

Star	R.A. h m	Dec. ° '	Date 1900+	p °	d "	M.E.D.	Δm	
h5094 .. 34°8332	.. 19 06.2	34 01	45.666 45.694 45.680	193.6 192.9 193.2	22.01 21.95 21.98	290 : 2 290 : 2	0.2 0.2 0.2	2n
h5117 .. 44°9569	.. 19 21.2	44 05	45.666 45.685 45.732 45.694	261.5 260.6 260.8 261.0	6.23 6.18 6.07 6.16	290. .2 290. .2 290. .3	1.5 2.0 2.0 1.8	3n
h5140 .. 65°3825	.. 19 40.4	65 09	42.653 42.710 42.682	83.7 82.4 83.0	1.93 2.05 1.99	290. .2 290. .2	-0.1 0.0 0.0	2n
h5163 .. 63°4561	.. 19 56.2	63 20	45.688 45.751 45.720	251.1 250.5 250.8	1.52 1.50 1.51	520. .3 520. .3	0.7 0.7 0.7	2n
β 763 .. 42°9068	.. 20 17.1	42 45	45.688 45.751 45.720	233.9 234.1 234.0	1.15 1.12 1.14	520. .4 520. .3	0.5 0.8 0.6	2n
Jc18 .. 40°9315	.. 20 27.1	40 54	42.724 42.762 42.743	224.6 225.0 224.8	4.79 4.38 4.58	290 : 2 290 : 3	0.7 0.5 0.6	2n
β 153 .. 26°7103	.. 20 41.4	26 47	47.719 47.722 47.881 47.774	265.5 264.8 267.9 266.1	1.64 1.64 1.64 1.64	420. .4 420. .3 420 : 2	1.0 2.0 2.0 1.7	3n
Rmk26 .. 62°6180	.. 20 43.3	62 48	42.800 45.732 45.770 44.767	86.0 87.2 89.8 87.7	2.71 2.67 2.75 2.71	290. .2 290. .2 290. .2	0.2 0.3 0.1 0.2	3n
h5246 .. 55°9530	.. 21 03.1	54 59	45.688 45.795 45.742	128.0 129.3 128.6	3.56 3.58 3.57	520. .4 290. .3	0.1 0.1 0.1	2n
Mlb6 .. 43°9451	.. 21 20.6	42 59	45.732 45.751 45.770 45.751	147.0 146.2 147.8 147.0	2.97 3.01 3.17 3.05	290 : 2 290. .3 290 : 2	2.0 2.5 2.0 2.2	3n
λ 466 .. 40°9649	.. 21 59.0	40 11	45.803 45.828 45.816	259.9 256.9 258.4	2.05 2.14 2.10	520. .3 290. .2	0.5 1.0 0.8	2n
HN56 .. 21°8078	.. 22 08.8	21 34	45.809 46.862 46.336	116.3 114.7 115.5	5.17 5.21 5.19	290. .1 300. .1	1.0 1.3 1.2	2n
I136 .. 45°10295	.. 22 19.9	45 37	42.820	271.3	1.97	290. .2	1.0	1n
I304 .. 48°10811	.. 22 40.9	48 50	45.770 45.795 45.782	357.8 360.0 358.9	4.63 4.45 4.54	290 : 2 290 : 3	1.5 1.5 1.5	2n
Δ 246 .. 51°11908	.. 23 01.5	50 14	42.820 45.803 44.312	256.4 257.1 256.8	8.76 8.77 8.76	290. .2 290. .2	0.3 0.2 0.2	2n

Star	R.A. h m	Dec. ° '	Date 1900+	p °	d "	M.E.D.	Δm	
$\Delta 247$ 23 12.1	61 33	45.809	288.9	45.50	290. .1	0.5	
$61^{\circ}6735+4$			46.862	289.2	45.85	300. .1	0.5	
			46.336	289.0	45.68		0.5	2n
$\Delta 251$ 23 34.1	47 12	45.828	274.7	4.17	290. .2	0.2	
$47^{\circ}10023$			46.862	274.4	4.26	300. .2	0.2	
			47.881	274.4	4.00	420. .3	0.2	
			46.857	274.5	4.14		0.2	3n

Notes.

Star	R.A. h m	Date	
$\beta 343$ 13 46.3	44.431	p presumably in error by 180° .
$\text{Slr}19$ 14 01.2	44.494	p changed by 180° .
$h4728$ 14 58.3	42.499	p changed by 180° .
$h5014$ 17 59.6	47.708	and 47.722 p changed by 180° .
$\beta 153$ 20 41.4	47.881	measured at hour angle $+2.1h$.

A CELL FOR AN 11½-INCH LENS.

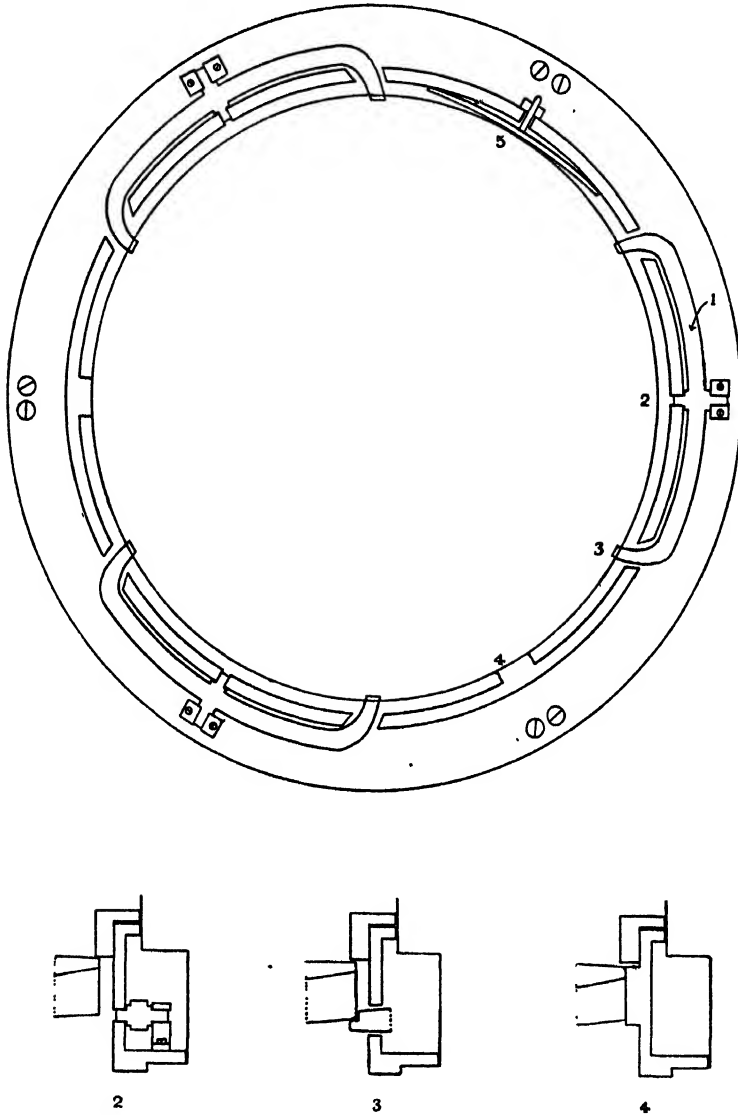
By HARLEY WOOD, M.Sc.

Manuscript received, January 6, 1948. Read (in title only), April 7, 1948.

The 11½-inch equatorial telescope was purchased for observation of the transit of Venus in 1874. The performance of the lens has never been really satisfactory and several attempts have been made to improve it (e.g. Russell, 1878). The lens, of the Fraunhofer type, has been subject to trouble arising from flexure. It was supported at three points and the crown lens was separated from the flint by three pieces of foil just of sufficient thickness to prevent contact of the components at the centre. On nights of good seeing the central discs of star images viewed through the lens were distinctly triangular and the diffraction rings either at the focus or extrafocal showed the same feature. The position angles of the vertices of the triangle remained the same relative to the points of support irrespective of the orientation of the components in the cell. In some positions of the crown on the flint there is a conspicuous astigmatism. It was with the idea of removing the effects of flexure that the lens mounting described below was designed. With the lens in the new cell and the relative positioning of the crown and flint arranged to reduce to a minimum the astigmatism which has been mentioned the performance of the lens is much improved and the triangularity of the diffraction pattern has disappeared. Previously there was some fear that the character of the images might give rise to systematic error in fine micrometric work such as the measurement of double stars, but no such feeling exists with the new arrangement.

In the figure the innermost circle represents the lens supported at six points round its circumference on the tips, 3, of three levers, 1, pivoted at 2. The lateral support of the lens consists of two fixed arcs, 4, and a spring, 5, capable of maintaining a pressure of fifteen pounds, approximately equal to the weight of the lens. A screw is fastened to the back of this so that it may be pulled back slightly to enable the lens to be placed in or removed from the cell. The spring, lined with velvet, has a ridge along the back which enables it to rock on the cell wall, so that when released it presses on the side of both components of the lens. The cell is attached to the telescope by three screws and three pushing screws are provided to enable it to be squared accurately on to the end of the telescope. The smaller figures below the main one give radial sections through the cell at the points marked 2, 3 and 4 and show the pivot, the lever projecting under the lens and the fixed lateral support. Also shown in these drawings is the light metal covering, which excludes dust from the lever system and the interior of the telescope, and the ring in the top of the cell which retains the lens. The ring is cut away except at three points round the cell near the pivots and is adjusted by three pairs of screws so that it just fails to be in contact with the crown component. The crown component is now separated from the flint by three solid metal leaves (0.28 mm. thick) and three thin springs placed alternately

around the lens at points corresponding to those where the flint is supported on the lever system. The springs are honed down so that each supports approximately one-sixth of the weight of the crown. The cell was made by E. W. Esdaile.



This way of mounting lenses should be useful for much larger sizes. In cases where the two components of a lens were separated the lower one might be supported by a double-ended lever system like this one and the upper one made more readily adjustable relative to the lower by using three weighted levers and three adjustable points of support.

REFERENCE.

Russell, H. C., 1878. *THIS JOURNAL*, 12, 247.

THE PARACLOACAL (ANAL) GLANDS OF *TRICHOSURUS VULPECULA*

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With Plates III-VI.

Manuscript received, March 1, 1948. Read, April 7, 1948.

William Cowper (1704), who gave the world the first description of the urogenital tract of a male marsupial (*Didelphys virginiana*), made the following statement in describing the muscles on the lower abdomen :

“Immediately under the skin about the cloaca I found a thin fleshy muscle enclosing the preputium and lower part of the rectum and odoriferous bags, together with four mucous glands at the root of the penis . . .”

These odoriferous bags no doubt refer to all or some of the glands which subsequently were called anal glands,† a name apparently used for the first time by Daubenton (ca. 1750), who mentioned the occurrence of a pair of anal glands in *Didelphys virginiana*. Subsequently these glands were noted in marsupials by Carus (1840), Michel St. Ange (1856), Garrod, Brass (1880), Widersheim (1893), Eggeling (1893), Disselhorst (1897), Hill (1899) in a wide variety of marsupials as pointed out by Van den Broek (1904). This last-named author gave us a detailed description of these glands referred to by him as rectal glands of the female of *Halmaturus* sp., *Petrogale penicillata*, *Cuscus orientalis* and *Sminthopsis crassicaudata*. He summarized his findings as follows :

On both sides of the lower part of the rectum and the cloaca are present three types of glands :

- (1) Tubular cloacal glands, which are branched tubular glands lined by simple cylindrical epithelium. They occur in the wall of the cloaca and in some species even higher up in the rectum and urogenital canal.
- (2) Hair follicle glands, which are complex branched sebaceous glands.
- (3) Rectal glands (anal glands). One pair only of these extraordinarily developed modified sebaceous glands occur. They are cell-producing structures but the secretion does not liquefy as in ordinary sebaceous glands.

In 1910 Van den Broek briefly referred to the rectal glands of male marsupials, particularly *Hypsignathus*, and classified these structures as accessory sex organs but adhered strictly to the term rectal glands. He stated on this occasion that they occurred in two pairs, of which in some species only the caudally situated pair developed.

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† As far as we are aware, previously no other author has referred to Cowper's observation in connection with these glands.

The work of Van den Broek suffered from the disadvantage that in Holland he usually had at his disposal one specimen only of each species examined. These specimens were sometimes unsatisfactorily preserved. This led to certain anatomical inconsistencies and no physiological aspects could be studied.

In spite of these drawbacks and the necessary incompleteness of Van den Broek's work executed some forty years ago, no further detailed account on the glands has been published since. McKenzie (1919), in his monograph on the urogenital tract of marsupials, referred to two sebaceous glands in the rectal region of *Trichosurus vulpecula* and also to a pair of ductless sex glands. Schaffer planned an extensive investigation on anal and related glands in general. However, only an introductory article on the history of the subject (1924) and some small references in an article on skin glands (1925) have been published as far as can be ascertained. Schaffer (1925) proposed the term paraproctal glands for these structures.

In the urine of *Trichosurus vulpecula*, Bolliger and Whitten (1940) observed spherical refractile bodies which subsequently were shown to originate from some of these glands. This observation led to the present study of these structures, which shall be referred to as paracloacal glands. They will be further subdivided into (a) scent or oil secreting, and (b) cell secreting glands, and an attempt shall be made to clarify in at least one species, *Trichosurus vulpecula*, the anatomical and functional position of these glands which may well be considered a marsupialian characteristic.

EXPERIMENTAL.

Forty living specimens of *Trichosurus vulpecula*, the common Australian phalanger or possum, of both sexes and different ages were examined. The paracloacal glands were palpated and their contents repeatedly expressed. The urine of these animals was also investigated. About 20 of these animals were killed or died and the glands were examined macroscopically and microscopically. The sections were stained with hæmatoxylin and eosin and with Sudan IV (Fett Ponceau).

In addition, glands of this nature were examined in living and dead specimens of *Pseudocheirus laniginosus*, *Macropus robustus*, *Petaurus papuanus* and *Perameles nasuta*.

FINDINGS.

(a) The Scent or Oil Secreting Glands.

I. Morphology.

Macroscopic: In *Trichosurus vulpecula* of both sexes a pair of egg-shaped glands about 0.5–1.5 cms. long and weighing about 0.4–1.5 gms. in the adult lie obliquely along the lateral walls of the rectum, with the larger end caudad and with the inferior extremity attached to the rectal wall by means of fibrous tissue. These glands can readily be palpated in the living specimen and are easily movable over the caudal rim of the pelvis about 1 cm. from the pubic symphysis. They are larger in males than in females. Each gland is a hollow viscus, the wall of which is 1–2 mms. thick. It floats on water.

A fine duct leaves each of these glands on the mesial inferior aspect and passing caudally penetrates the cloacal wall and opens into the interior of that organ about 2–3 mms. from the cloacal rim. (Plate III and Plate IV, Fig. 1.)

Microscopic: The gland wall consists of the following layers: (1) The secreting epithelial layer, (2) a lamina propria, and (3) a muscular tunic. (Plate IV, Fig. 2.)

The epithelial layer is thrown into many folds. The major folds are subdivided into smaller folds. The number of folds varies considerably in different animals and also depends to some degree on the distention of the gland cavity. The epithelium is several cells thick and consists of large cuboidal or polygonal cells. The cytoplasm of these cells is granular and stains pink with eosin. In some instances the cytoplasm is foamy in appearance. Many of these foamy cells are seen in different stages of disintegration. The nuclei are round and have a well defined membrane and a nucleolus. Particularly in the cells with foamy cytoplasm the nuclei are frequently pyknotic and crenated or are completely absent. (Plate V, Fig. 1.) These cells separate from the epithelium and disintegrate to form a secretion consisting of oil droplets of relatively uniform size dispersed in a small amount of aqueous medium.

On staining frozen sections with Sudan IV nearly all the epithelial cells close to the lumen are covered with strongly red staining granules. The lamina propria is sparse, and adjacent to the muscular layer contains cavities with single columnar epithelial lining which resemble ducts of sweat glands.

The muscular coat consists of a few circular bundles which are greatly reinforced by longitudinal fibres on one of the lateral surfaces. These fibres are striated (voluntary muscle).

II. *Physiology.*

(a) *Secretions from the Scent or Oil Producing Glands.* The contents of the oil producing glands consist of a cream coloured oily liquid (about 0.5–1.0 ml.) which has an unpleasant odour resembling that of rotten onions or garlic. On microscopic examination this liquid is found to consist of oily droplets emulsified in an aqueous phase. On drying this emulsion in the desiccator a white semi-solid stays behind. This substance though not soluble in water is markedly hygroscopic and gives a strongly positive Burchhardt-Liebermann reaction indicating the presence of cholesterol or cholesterol esters. The nature of the contents of these glands may therefore be well considered as some form of sebum which is ultimately secreted from the gland through a fine duct whose opening is about 2 mms. from the cloacal rim. Frequently this secretion can be demonstrated on the intact animal by pressing on the oil-producing gland. The creamy secretion with its characteristic odour can be seen appearing on the orifice of the duct and recognised by its odour. The administration of adrenalin or pilocarpin did not bring on a secretion. However, in handling certain animals and in the ensuing struggle secretion frequently occurs and can be obtained from the orifice near the cloacal rim. These animals usually empty their bladder on this occasion and the secretion is detected in the urine by its strong odour. On the other hand, no secretion can be obtained from the oil-producing gland from many struggling animals or even by pressing on the gland, though the typical secretion can still be aspirated from the glands directly by puncturing the wall with a fine hypodermic needle. In these instances it appears as though the narrow duct were blocked, perhaps by inspissated secretion. In animals dying rather suddenly as, for example, after the administration of an overdose of an anaesthetic, a copious secretion from the oil glands nearly always occurs. If dying slowly from disease, this secretion does not occur.

(b) *The Effect of the Surgical Removal of the Scent Glands.* The scent glands can be readily amputated through a skin incision and in consequence no further secretion from the ducts is noticed. After observing two animals for over six months, no irregularities in defaecation were noticed and the general health of the animals did not suffer from this operation. The glands did not reform from the unexcised ducts.

*(b) The Cell Secreting Glands.**I. Morphology.*

Macroscopic : Caudally but very close to the scent glands another pair of glands occurs in both sexes which is palpable on the lateral wall of the cloaca about 1 cm. from the external orifice just beneath the mucosa. They are firmly attached to the surrounding tissue. These bodies are spherical or heart-shaped and usually are bi-lobed, though in two specimens they were found to contain three lobes. One gland of one animal consisted of one lobe only. In all cases, however, the lobes are enclosed by a common capsule, the outline of which indicates the subdivisions of the enclosed gland. In contrast to the scent glands these glands do not float on water. Each lobe of these glands is provided with a duct about 1 cm. long which traverses the cloacal wall obliquely to open on each side of the duct of the oil producing gland and about 1 mm. from it. These two or three fine ducts are often remarkably pigmented and almost black at the orifice. Thus we usually find on the lateral aspects of the cloacal wall three ducts parallel to each other and opening about 0.2 cm. above the external orifice of the cloaca. The central opening which is from the scent gland is not or is only slightly pigmented and more difficult to see. (Plate III and Plate IV, Fig. 1.)

Microscopic : The wall of each lobe of the cell producing gland also consists of three elements : (1) the secreting epithelial layer, (2) a lamina propria, and (3) a muscular tunic.

Superficially, the secreting epithelial layer has a somewhat similar appearance to that of the scent gland, but is usually thicker, leaving less unoccupied space in the interior of the glands. (Plate V, Fig. 2).

The large pink staining polygonal cells (30 μ diam.) also have a granular cytoplasm which may become quite foamy in appearance in the cells nearer the surface. Furthermore, some cells on the surface of the epithelium are ovoid in shape and with a cytoplasm consisting of only a fine reticulum. On the other hand, the cell membranes of these apparently dying cells are thickened, sharply defined and refractile. (Plate VI, Fig. 1.) These cells are encountered in the interior of the glands, in and at the orifices of the pigmented ducts and ultimately in the urine. (Plate VI, Fig. 2.) As in the scent glands, the cell nuclei are round in general, have a well-defined membrane, and a nucleolus. Some nuclei in the faintly staining foamy cells with a well-defined membrane are pyknotic and crenated, but they are frequently still present when the cell has separated from the epithelium. Subsequently, these nuclei disappear.

The interior of a number of these cells just before or after being cast off from the epithelium contains large granules which stain red with Sudan IV. All the other epithelial cells, however, possess only small and faintly fat staining granules. The cast off cells obtained in the secretion of the ducts or in the urine practically always contain fat droplets covering the greater part of the cell and staining strongly with Sudan and Osmium. In the unstained specimen these fat droplets frequently give the cell the appearance of a parasitic ovum.

The lamina propria is better developed than in the oil glands. In addition to a thin layer of muscle surrounding the whole gland each lobe has its own muscular layer which frequently becomes very pronounced between adjacent lobes.

Tubules lined with a single columnar epithelium which resemble ducts of sweat glands are seen in the muscular layer close to the epithelium.

II. Physiology.

As pointed out previously, the desquamated cells from the cell producing glands do not liquefy and form the major part of a secretion consisting of these

cells suspended in a small volume of an aqueous medium. This secretion unlike that of the scent gland has no marked odour. It passes down the two ducts from each gland and becomes deposited inside the cloaca but very close to its rim, and whenever the animal urinates it is washed away with the stream and is practically always found in the urine.

These cells remain intact for several weeks even if the urine putrefies. They have been observed in the urine of the young *Trichosurus vulpecula* as soon as it leaves the pouch of the mother, and generally speaking they are present in exceptionally large amounts in immature animals of both sexes, viz. 5-20 cells in a dry low power field. In adult specimens they are more numerous in males than in females. In females they can sometimes only be found after examining many fields or in the centrifuged sediment.

On defæcation the appearance of cell and oil gland secretion may be seen because the rim of the cloaca becomes sufficiently everted to allow the orifices of the ducts to open externally. On this occasion these secretions may be deposited on the fæces.

The Effect of the Surgical Removal of the Cell Producing Glands. Through a skin incision the cell producing glands (which are firmly attached to the surrounding tissues) can be dissected out quite readily. No further secretion typical of these glands can be noticed for several months. After about six months, however, signs of testicular degeneration were noted in several animals, but it is felt that the number of experiments is too small as yet to draw any definite conclusions.

Other Marsupials Examined.

Macropus robustus (Kangaroo).

On a formalin preserved specimen (male) the findings of Van den Broek were confirmed in that only one pair of glands were present and the duct which is 2 to 3 cms. long, opens into the rectum about 1 cm. from the cloaca. The cloaca, however, differs from that of the other species examined in that it is sparsely provided with hairs.

Perameles nasuta (Bandicoot).

In the bandicoot also only one pair of glands was found. These glands produced a cellular secretion and their ducts opened within 1 mm. of the dorso-lateral margin of the cloaca. The cloaca was similar to that of *Trichosurus vulpecula* and *Pseudocheirus laniginosus* in that it was without hairs.

Pseudocheirus laniginosus (Ring-tailed Possum).

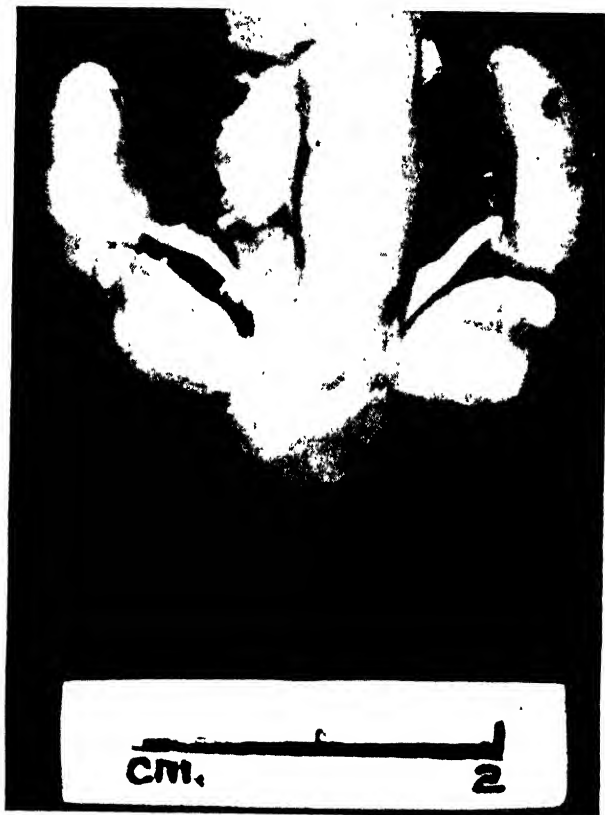
There are two pairs of glands, as in *Trichosurus vulpecula*, but both produce an oily secretion without any cellular elements.

Petaurus papuanus (New Guinea Flying Phalanger).

Two pairs of paracloacal glands could be palpated in the living animal, but only oily droplets and no typical cell gland bodies could be found in the urine.

DISCUSSION.

The anatomy of the hind end of marsupials is different from that of higher mammals and this makes it difficult to label the glands situated in the characteristic conically shaped cloacal hillock in terms of general mammalian anatomy. They have variously been called rectal, anal and paraproctal glands by different authors. All these terms, however, imply that these glands are connected with the lower end of the intestinal tract. However, this assumption



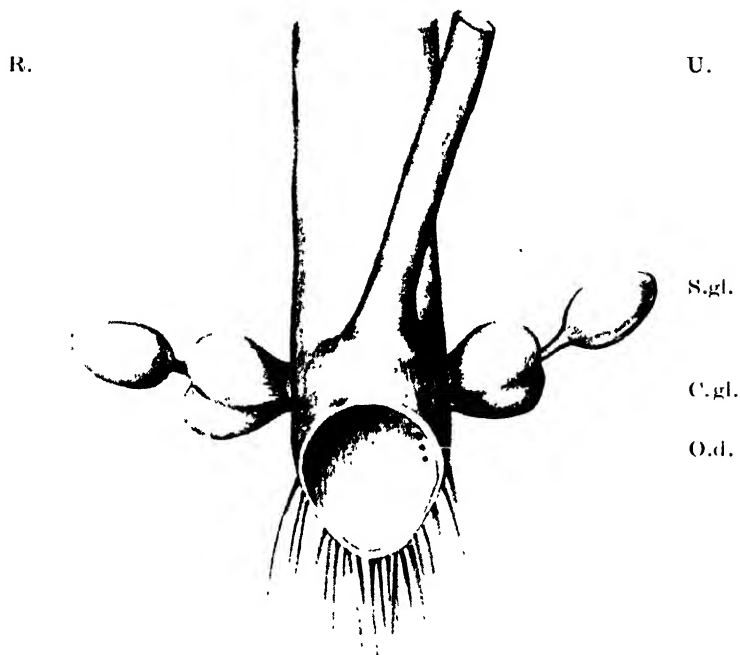


Fig. 1.

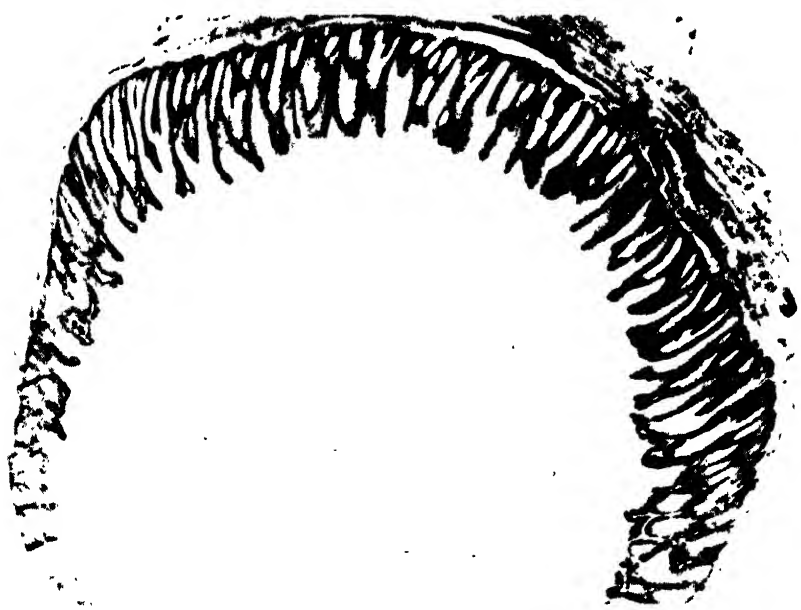


Fig. 2.



Fig. 1.

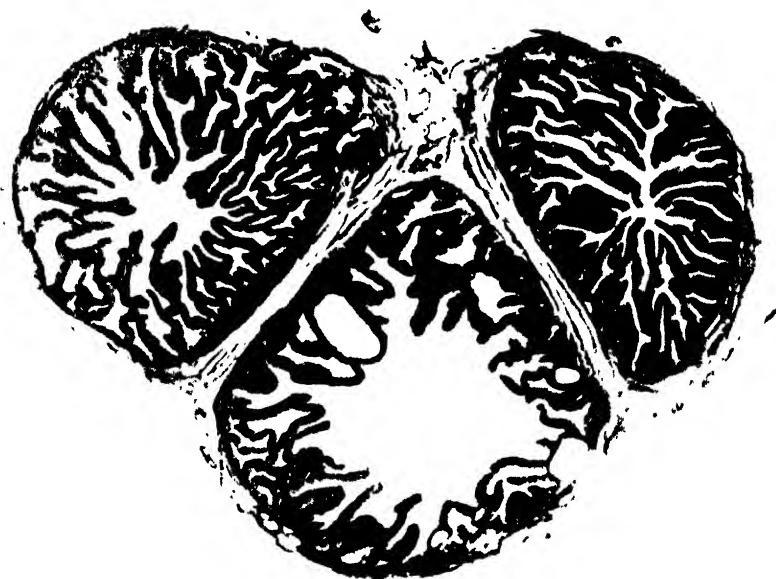


Fig. 2.

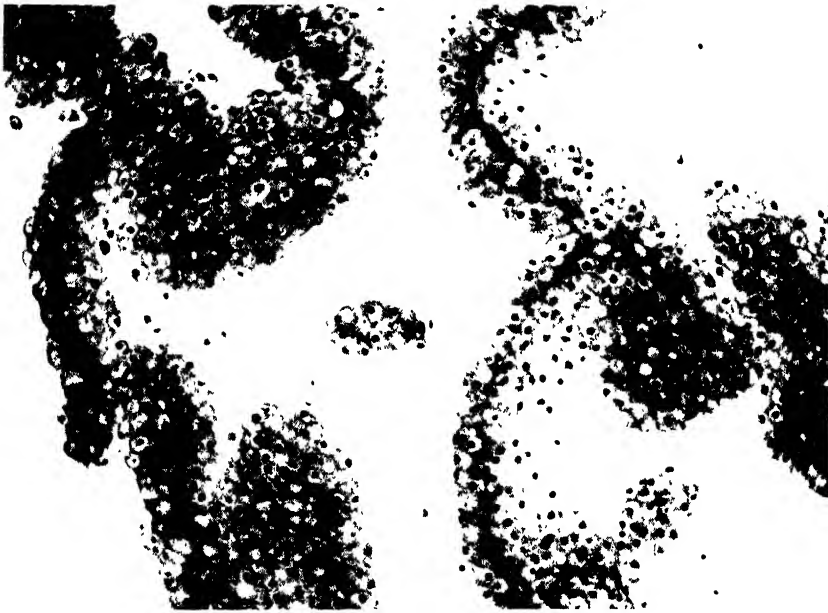


Fig. 1.



Fig. 2.

has not yet been proven in any way and the possibility that some of these glands may for example correspond to the prepuccial glands of eutherian mammals cannot be wholly excluded. Therefore, it was decided to name them paracloacal glands, a non-committal term. It is realized, however, that some of the fully grown marsupials do not possess a cloaca, as for example *Didelphys virginiana*, where the ducts of at least one pair of these glands open exteriorly besides the anal rim. The new terms "cell and oil producing glands" are self-explanatory (though somewhat clumsy).

Originally Van den Broek (1904) recognized only one pair of these glands as true rectal glands, the specific term used by this author for what we term paracloacal glands. In a subsequent publication (1910) dealing with the structure of the male reproductive organs he postulated the occurrence of two pairs of rectal glands in marsupials, but only one pair may develop fully, as in the case of *Macropus* sp. However, he also states that the occurrence of one pair of glands is a characteristic of Phalangeridæ, which in this paper is shown to be incorrect in the case of both sexes of *Trichosurus vulpecula* and *Pseudocheirus laniginosus*. Only on one occasion we found a phalanger which presented a single pair of fully developed glands. These glands were of a peculiar structure and could not be classified definitely as either cell or oil glands. The specific pair of "rectal" glands, by Van den Broek's original definition, corresponds to the cell producing glands as described by us in detail in *Trichosurus vulpecula*. The Dutch author described them as extraordinarily well developed and modified sebaceous glands. In his sections of these structures he noticed that the cells secreted by them do not liquefy as in ordinary sebaceous glands, and he expressed the opinion that the purpose of these glands consisted in lubricating the terminal section of the rectum and cloaca in order to facilitate the passage of the faecal bolus.

Our investigations on *Trichosurus vulpecula* confirmed the cell producing function of these glands. They further brought out the fact that these cells are secreted fairly continuously and are washed away from the cloacal wall by the urinary stream and are found in the urine. It is these cells from the cell producing glands which give the urinary sediment of *Trichosurus vulpecula* and certain other marsupials, these characteristic bodies frequently resembling ova of parasites and whose nature is now explained for the first time.

In the case of the possum it is hardly feasible to assume that this cellular secretion has a lubricating action in the process of defæcation because before the faeces leaves the extended anus it is in no way in contact with the openings of the ducts from these glands. The as yet unexplained nature of the cell producing glands has been studied by removal and endocrine experiments which seem to indicate that these structures respond as if they were accessory sex glands and probably also necessary for gonad maintenance.

The fact that the cells of the cell producing gland do not liquefy as they usually do in sebaceous glands might have an analogy in the prepuccial glands of an eutherian mammal, the weasel (*Putorius nivalis*), in which the lining also consists of a stratified epithelium whose surface cells are detached and secreted as such (Schaffer, 1925). However, it has to be pointed out that these prepuccial glands are without ducts and open directly on to the surface of the fold. Nevertheless, the papillæ and crypts of these glands closely resemble those of the paracloacal glands.

On the basis of Van den Broek's findings Schaeffer (1925) suggests that these holocrine glands arise from definite epidermal areas which have been detached from the surface of the body and become located subcutaneously in the modified form of large encapsulated gland bodies with long ducts. The epidermal nature is demonstrated by the high papillæ which project into the broad squamous

epithelium of the gland. This conception is supported by the observation that typical sweat gland structures are found in the walls of these glands. Van den Broek (1904) apparently referred to these structures as tubular cloacal glands. The continuous desquamation of cells may be considered a further epidermal characteristic.

In spite of a superficial similarity the scent or oil producing glands differ histologically from the neighbouring cell glands and in *Trichosurus vulpecula* a definite functional difference lies in the fact that the cells secrete and liquefy and the liquid secretion formed has an unpleasant odour. This property seems to place the scent glands of *Trichosurus vulpecula* and other marsupials amongst the scent glands met with in many species of mammals in general. They appear to be definitely related to the defence of the animal and they also may play a rôle in the sex behaviour.

SUMMARY.

The large glands in the subcutaneous tissue of the cloacal hillock of *Trichosurus vulpecula* and other marsupials have been examined anatomically and physiologically. They are referred to as paracloacal glands.

The two pairs present in both sexes of *Trichosurus vulpecula* have been subdivided according to their activity into a pair of oil producing or scent glands and a pair of cell producing glands.

The individual oil producing gland is a single hollow viscus. Its main function seems to be that of a scent gland.

The cell producing gland is usually a bilobed or trilobed structure. Its function remains obscure. These glands do not liquefy their cellular secretion which ultimately appears in the urine as cells. This phenomenon has so far not been encountered in eutherian mammals.

Histologically all these glands are of a sebaceous nature. However, definite differences exist between the epithelial layers of the two glands.

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EXPLANATION OF PLATES.

PLATE III.

Dissection illustrating the egg-shaped scent glands and the bi-lobed cell-producing glands in a male *Trichosurus vulpecula*. Note the ducts from the scent glands entering the wall of the cloaca close to the caudal end of the cell-producing glands. The material for this dissection was hardened in formalin. Posterior aspect.

PLATE IV.

Fig. 1.—Semidiagrammatic drawing from freshly dissected material illustrating the scent and cell-producing glands of a female *Trichosurus vulpecula*. Anterior view. In order to show the relationship between the orifices of the ducts and the rim of the cloaca the cloacal opening is depicted in a distended state.

R.=rectum. U.=Urogenital canal. S.gl.=Scent gland. C.gl.=Cell-producing gland. O.d.=Orifices of ducts.

Fig. 2.—Cross section of part of the scent or oil-producing gland obtained from fully grown male *Trichosurus vulpecula*. The photograph demonstrates the folded epithelium and the reinforced muscular layer on one of the lateral surfaces. (×6.) Stained with hæmatocrylin and eosin.

PLATE V.

Fig. 1.—Epithelial layer and *lamina propria* of scent gland. Note the cuboidal or polygonal cells and their nuclei. ($\times 100$.) Stained with hæmatoxylin and eosin.

Fig. 2.—Cross section through a trilobed cell-producing gland obtained from a female *Trichosurus vulpecula*, who had received injections of testosterone. The strongly developed epithelium resembles that of a normal male. ($\times 6$.) Stained with hæmatoxylin and eosin.

PLATE VI.

Fig. 1.—Microphotograph of some of the papillæ of the cell-producing gland epithelium. Note the well defined membrane of the dying cells. ($\times 100$.) Stained with hæmatoxylin and eosin.

Fig. 2.—Cellular secretion from the cell-producing glands of a fully grown female *Trichosurus vulpecula*. The specimen which was obtained from the orifices of the ducts is unstained. It has, however, been diluted with water in order to obtain individual cells. ($\times 400$.)

A SURVEY OF ANTHOCYANINS IN THE AUSTRALIAN FLORA.

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INTRODUCTION.

The synthetical work on the anthocyanin pigments by Robinson and his school led to the development of methods of identification of individual anthocyanins in solution in plant extracts (Robinson and Robinson, 1931, 1932, 1933, 1934; Lawrence, Price, Robinson and Robinson, 1938). The relative ease of identification has made possible large-scale surveys of the distribution of anthocyanins in plants, and particularly in flowers (Lawrence, Price, Robinson and Robinson, 1939; Taylor, 1940; Beale, Price and Sturgess, 1941), which have had as their main objective the elucidation of the biosynthesis of the anthocyanins. Genetical investigations bearing on this and other problems have also been facilitated (Scott-Moncrieff, 1939; Beale, 1941). The information collected in the surveys may in addition have some value to phylogenetics.

A large proportion, probably the majority, of the plants examined in these surveys had been cultivated in gardens for many years and it may be expected that the distribution of anthocyanins in such plants is affected by artificial selection, preservation of mutant forms and hybridisation. We have therefore carried out a survey of the occurrence of anthocyanins in the flowers of some 300 native Australian species, including some tropical species from New Guinea, together with a smaller number of fruits. Approximately 20% of the species investigated were cultivated, and the results for these have been analysed separately. All available anthocyanin-containing species, both wild and cultivated, were examined irrespective of size or colour.

The list of species examined is set out in Table 1. As in previous surveys, the botanical classification used is that of Hutchinson (1926), arranged in reverse order so that the more highly developed plants are placed first.

TABLE 1.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.

- (i) Mode of occurrence of anthocyanin in the flower or fruit.
 (ii) Colour of anthocyanin in the flower or fruit.
 (iii) Anthocyanidin.
 (iv) Glycoside type.
 (v) Distribution of the species along the east coast of Australia (or New Guinea or Western Australian species).

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.					
LAMIALES.					
LABIATÆ (76-264).					
<i>Ajuga australis</i> R.Br. . . .	A†	Blue	Delph.	PG.	G.
<i>Hemigenia purpurea</i> R.Br.	A	Red/Blue	Delph.	Dimon.	33/36
<i>Plectranthus parviflorus</i>					
Henck.	A	Red/Blue	Cyan.	Dimon.-A	G.
<i>Prunella vulgaris</i> Linn. . .	A†	Red/Blue	Malv. (Fe +)	PG.	ST/Tm.
<i>Prostanthera lasiantha</i>					
Labill.	Bb	Red/Blue	Malv.	Digly.	ST/Tm.
<i>P. linearis</i> R.Br.	A	Blue	Delph.	Dimon.	ST.
<i>P. ovalifolia</i> R.Br.	A*	Blue	Malv. X	(Note 11)	ST.
<i>P. Sieberi</i> Benth.	A*	Blue	Cyan.	Bios.	33/36
<i>P. sp.</i>	A	Blue	Malv. X	Dimon.	
<i>Westringia rosmariniformis</i>					
Sm.	Bc	Red/Blue	Malv.	Digly.	ST/Tm.
VERBENACEÆ (76-263).					
<i>Clerodendron tomentosum</i>					
R.Br.	Calyces	Red	Peon.	A-sugar	Tr/ST.
<i>C. sp.</i>	A	Red	Pel.	Bios.	NG.
<i>Duranta Plumieri</i> Jacq. . .	A	Red/Blue	Malv.	Mon.	NG.
<i>Faradaya sp.</i>	A	Red	Peon.	Mon.	NG.
<i>Premna integrifolia</i> Linn.	Fruit	Blue/Black	Malv.	Mixture	NG.
<i>Stachytarpheta dichotoma</i>					
Vahl.	A	Blue	Malv.	Digly.	NG.
PERSONALES.					
ACANTHACEÆ (75-259).					
<i>Eranthemum variabile</i> R.Br.	A†	Blue	Malv.	PG. ?	Tr/ST.
<i>Graptophyllum Earlii</i>					
F. Muell.	A*	Red	Pel.	Mon.	Tr.
BIGNONIACEÆ (75-257).					
<i>Tecoma australis</i> R.Br.	Bb	Red	Cyan. + Peon.	PG.	G.
<i>Tecomathe dendrophilia</i>					
K. Schum.	A	Red	Malv.	Mon.	NG.
Unidentified sp.	Bb	Red/Blue	Cyan.	Bios. ?	NG.
LENTIBULARIACEÆ (75-254).					
<i>Utricularia dichotoma</i> Labill.	A	Red/Blue	Delph.	Dimon.	ST/Tm.
SCROPHULARIACEÆ (75-252).					
<i>Veronica Derwentia</i> Littlej.	A†	Blue	Nitro- genous ?	(Note 7)	ST/Tm.
SOLANALES.					
CONVOLVULACEÆ (74-251).					
<i>Convolvulus sepium</i> Linn.	Bb†	Pink	Cyan.	Dimon. (11)	ST/Tm.
<i>C. sepium</i> Linn. var.					
<i>Soldanella</i>	A	Red/Blue	Cyan.	Mon.	ST/Tm.
<i>Ipomœa congesta</i> R.Br.	Ba	Red/Blue	Peon.	Bios. ?	NG.
<i>I. Pes-capræ</i> Roth. (Note 5)	A	Red/Blue	Cyan.	Mon.	Tr.
<i>I. Quamochit</i> Linn.	A	Red	Cyan.	PG.	NG.
<i>I. sp.</i>	A	Red/Blue	Cyan.	Bios.	NG.
<i>Polymeria calycina</i> R.Br.	A	Pink	Malv.	Mixture	ST.

TABLE 1.—Continued.
Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
SOLANALES.—Continued.					
SOLANACEÆ (74–250).					
<i>Solanum aviculare</i> Forst.	A	Blue	Nitro- genous ?	(Note 8)	ST/Tm.
<i>S. campanulatum</i> R.Br. . .	A	Blue	Pet. + Malv.	Dimon.	ST.
<i>S. nigrum</i> Linn.	Fruit	Blue/Black	Malv. X	Mixture	G.
<i>S. stelligerum</i> Sm. . . .	A	Blue	Pet. + Malv.	Dimon.	Tr/ST.
<i>S. vesicum</i> F. Muell. . .	A	Blue	Malv.	Dimon.	ST/Tm.
Do.	Fruit	Blue	Malv.	Mixture	
CAMPANALES.					
STYLIDACEÆ (71–246).					
<i>Stylidium graminifolium</i>					
Swartz.	A†	Pink	Cyan.	Mon.	ST/Tm.
<i>S. lineare</i> Swartz. . . .	A	Pink	Cyan.	Mon.	ST.
GOODENIACEÆ (71–245).					
<i>Dampiera Brownii</i> F. Muell.	A	Blue	Delph.	Mixture	ST/Tm.
<i>D. stricta</i> R.Br.	A	Blue	Malv.	Mixture	ST/Tm.
<i>Goodenia (paniculata</i> Sm. ?)	Bc	Red	Malv.	Mixture	G.
<i>Scævola hispidula</i> Cav. . .	A	Blue	Delph.	Mixture	ST/Tm.
<i>S. (Hookeri</i> F. Muell. ?)	Ba	Red	Malv.	Bios.	Tm.
<i>S. microcarpa</i> Cav. . . .	A	Blue	Delph.	Dimon.	ST/Tm.
<i>S. suaveolens</i> R.Br. . . .	A	Blue	Delph.	Dimon.	G.
Do.	Fruit	Blue	Delph.	PG.	
LOBELIACEÆ (71–244).					
<i>Isotoma axillaris</i> Lindl. . .	A	Blue	Malv. X	Mixture	ST/Tm.
<i>Lobelia anceps</i> Thunb. . .	Bb	Blue	Malv. (Fe+)	PG.	ST/Tm.
<i>L. dentata</i> Cav.	A	Blue	Delph.	Bios.	ST.
<i>L. purpurascens</i> R.Br. . .	A	Blue	Malv. (Fe+)	Mixture	ST/Tm.
CAMPANULACEÆ (71–243).					
<i>Wahlenbergia gracilis</i> DC.	A†	Blue	Delph.	Dimon.	G.
ASTERALES.					
COMPOSITÆ (67–238).					
<i>Brachycome decipiens</i>					
J. Hook. or <i>B. scapiformis</i> DC.	Bc	Red/Blue	Delph.	Dimon.	ST/Tm.
<i>Erechthites valerianifolia</i> DC.	A	Red/Blue	Cyan.	Digly.	NG.
<i>Helipterum Manglesii</i>					
F. Muell.	Bracts	Pink	Peon. (11)	Bios.	WA.
<i>Humea elegans</i> Sm. . . .	A	Red/Blue	Peon.	Indef. (10)	Tm.
<i>Olearia dentata</i> Moench. . .	Bb	Blue	Malv.	Bios.	Tm.
<i>Vernonia cinerea</i> Less. . .	A†	Red/Blue	Malv. X	Digly.	G.
RUBIALES.					
RUBIACEÆ (66–232).					
<i>Opercularia aspera</i> Gaertn.	Bc	Red/Blue	Abnormal (9)		ST/Tm.
<i>Pomax umbellata</i> Sol. . .	Bc	Red	Delph.	PG.	G.
APOCYNALES.					
APOCYNACEÆ (65–230)					
<i>Ochrosia elliptica</i> Labill.	Fruit	Red	Cyan.	Bios.	Tr.
LOGANIALES.					
OLEACEÆ (64–229).					
<i>Olea paniculata</i> R.Br. . .	Fruit*	Blue/Black	Cyan.	Mon.	Tr/ST.
EBENALES.					
SAPOTACEÆ (61–222).					
<i>Sideroxylon australis</i> Benth.	Fruit	Blue/Black	Cyan.	PG.	Tr/ST.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
ERICALES.					
EPACRIDACEÆ (60–217).					
<i>Astroloma humifusum</i> R.Br.	A	Red	Cyan.	Mon.	Tm.
<i>Dracophyllum secundum</i> R.Br.	Ba	Red	Cyan.	PG.	33/36
<i>Epacris longiflora</i> Cav.	Ba†	Red	Cyan.	Mon.	Tm.
<i>E. longiflora</i> var. <i>superba</i> (3)	*	Red	Cyan.	Mon.	
<i>E. microphylla</i> R.Br.	Bracts	Red	Cyan.	PG.	ST/Tm.
<i>E. obtusifolia</i> Sm. (6)	B†*	Red	Cyan.	Mon.	ST/Tm.
<i>E. pulchella</i> Cav.	Bb	Red	Cyan.	Mon.	ST.
<i>E. reclinata</i> Cunn.	Ba†	Red	Cyan.	Mon.	33/36
<i>Leucopogon amplexicaulis</i> R.Br.	B	Red	Cyan.	Mon.	33/36
<i>L. pulchellus</i> Sond.	Bc	Red	Cyan.	Mon.	WA.
<i>Lissanthe sapida</i> R.Br.	Fruit	Red	Cyan.	Mon.	33/36
<i>L. strigosa</i> R.Br.	B†	Red	Cyan.	PG.	ST/Tm.
<i>Styphelia tubiflora</i> Sm.	A	Red	Malv. X	A-sugar	33/36
<i>Trochocarpa laurina</i> R.Br.	Fruit	Blue/Black	Cyan.	Mixture	Tr/ST.
<i>Woollsia pungens</i> F. Muell.	Bb†	Pink	Malv.	Mon.	ST.
UMBELLIFLORÆ.					
UMBELLIFERÆ (59–213).					
<i>Actinotus helianthi</i> Labill.	Bc	Red	Cyan. + Peon.	PG.	ST.
ARALIACEÆ (59–212).					
<i>Panax sambucifolius</i> Sieb.	Fruit	Blue	Malv.	Digly.	ST/Tm.
SAPINDALES.					
SAPINDACEÆ (57–198).					
<i>Dodonaea viscosa</i> Linn. var. <i>purpurea</i>	A*	Red	Cyan.	Mon.	
Do.	Fruit*	Red/Blue	Cyan.	Mon.	
<i>Nephelium leiocarpum</i> F. Muell.	Fruit	Red	Peon.	PG.	ST/Tm.
MELIALES.					
MELIACEÆ (56–197).					
<i>Melia azedarach</i> Linn. var. <i>australasica</i> DC.	A*	Red/Blue	Cyan.	Mon.	Tr/ST.
RUTALES.					
RUTACEÆ (55–194).					
<i>Boronia Bakeriana</i> F. Muell.	A†	Pink	Malv.	Dimon.	33/36
<i>B. elatior</i> Bartl. (3)	A*	Pink	Malv. (Trace Fe+)	Dimon.	WA.
<i>B. heterophylla</i> F. Muell.		Red	Malv.	Bios.	WA.
<i>B. ledifolia</i> Gay.	A	Pink	Malv.	Mon.	ST.
<i>B. ledifolia</i> var. <i>triphylla</i>	A	Pink	Malv.	Dimon.	33/36
<i>B. megastima</i> Nees	Bb*	Red	Delph. X (11)	Bios.	WA.
<i>B. microphylla</i> Sieb.	A	Pink	Malv. (some Fe+)	Dimon.	ST.
<i>B. pinnata</i> Sm.	A	Pink	Malv.	Dimon.	ST/Tm.
<i>B. polygalifolia</i> Sm.	A†	Pink	Malv.	PG.	ST/Tm.
<i>B. serrulata</i> Sm.	A†	Pink	Malv.	Dimon.	33/36
<i>Citrus australasica</i> F. Muell.	A†*		Malv.	Mon.	ST.
<i>Correa speciosa</i> Andr.	Ba†	Red.	Cyan.	PG.	ST/Tm.
<i>Correa speciosa</i> var. <i>ventricosa</i> (1)	*	Red	Cyan.	PG.	

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
RUTALES.—Continued.					
RUTACEÆ.—Continued.					
<i>Eriostemon Crowei</i> F. Muell.	A	Pink	Malv.	Mon.	ST/Tm.
<i>E. lanceolatus</i> Gaertn. ..	A	Pink	Malv.	PG.	ST/Tm.
<i>E. hispidulus</i> Sieb. ..	A†	Pink	Cyan. (+ Peon. ?)	Digly.	ST.
<i>Philotheca australis</i> Rudge	A	Red/Blue	Delph.	A-sugar	ST.
RHAMNALES.					
AMPELIDACEÆ (54–193).					
<i>Vitis hypoglauca</i> F. Muell. (4)	Fruit	Blue-Black	Malv.	Mon.	G.
CELASTRALES.					
STACKHOUSIACEÆ (51–181).					
<i>Stackhousia linarifolia</i> Cunn.	Bc		Malv. (Fe +)	Dimon.	ST/Tm.
URTICALES.					
MORACEÆ (50–167).					
<i>Ficus Bellingeri</i> C. Moore ..	Fruit*	Red	Cyan.	Mon.	ST.
<i>F. macrophylla</i> Desf. ..	Fruit*	Red	Malv.	PG.	ST.
<i>F. rubiginosa</i> Desf. ..	Fruit*	Red	Malv.	Mixture	ST.
<i>F. sp.</i>	Fruit	Red	Cyan.	Mon. or PG.	NG.
<i>F. sp.</i>	Fruit	Red	Cyan.	PG.	NG.
<i>F. sp.</i>	Fruit	Red	Cyan.	PG.	NG.
CASUARINALES.					
CASUARINACEÆ (49–164)					
<i>Casuarina Cunninghamiana</i> Miq.	A	Red	Malv. (Fe +)	Mon.	G.
<i>C. distyla</i> Vent.	A ♂	Red	Delph.	A-sugar	ST/Tm.
<i>Do.</i>	A ♀	Red	Delph.	A-sugar	
<i>C. glauca</i> Sieb.	A* ♂	Red	Cyan.	Mon.	ST/Tm.
<i>Do.</i>	A ♀	Red	Delph. + Cyan.	Mon.	
<i>C. nana</i> Sieb.	A ♂	Red	Cyan.	Mon.	Tm.
<i>Do.</i>	A ♀	Red	Delph. + Cyan.	Mon.	
<i>C. paludosa</i> Sieb. ..	A	Red	Cyan.	PG.	Tm.
<i>C. rigida</i> Miq.	A ♂	Red	Cyan.		ST/Tm.
<i>Do.</i>	A ♀	Red	Delph. + Cyan.	Mon.	
<i>C. suberosa</i> Ott. et Dietr.	A ♂	Red	Peon. + Cyan.	Mon.	G.
<i>Do.</i>	A ♀	Red	Cyan.	PG.	
LEGUMINOSÆ.					
PAPILIONACEÆ (41–148).					
<i>Aotus villosa</i> Sm. ..	Bb	Red/Blue	Malv.	PG.	ST/Tm.
<i>Bossia cinerea</i> R.Br. ..	Bb	Red	Cyan.	Dimon. (10)	Tm.
<i>B. ensata</i> Sieb.	Bb	Red	Malv.	Mon.	ST/Tm.
<i>B. heterophylla</i> Vent. ..	Bb	Red	Delph. (X ?)	Mixture	ST/Tm.
<i>B. microphylla</i> Sm. ..	Bb	Red	Malv.	Mon.	ST/Tm.
<i>B. prostrata</i> R.Br. ..	Bc	Red	Peon.	Mon.	ST/Tm.
<i>B. rhombifolia</i> Sieb. ..	Fruit	Red	Cyan.	Mon.	ST.
<i>Brachysema lanceolata</i> Meissn.	A*	Red	Cyan.	Mon. (10)	WA.
<i>Canvalia obtusifolia</i> DC. ..	A	Red/Blue	Malv.	PG. or Mon.	NG.
<i>Castanospermum australe</i> Cunn. et Fras. ..	Bb*	Red	Cyan.	Mon.	Tr.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
LEGUMINOSÆ.—Continued.					
PAPILIONACEÆ.—Continued.					
<i>Chorizema cordatum</i> Lindl.	Ba*	Pink	Malv.	Mon.	WA.
<i>Clanthus Dampieri</i> Cunn.					
(11)	A	Red	Pel. + Cyan.	Mon.	ST.
<i>Chitoria ternatea</i> Linn.	A	Blue	Delph.	Dimon.	NG.
<i>Daviesia corymbosa</i> Sm.	Bb	Red	Cyan.	Bios.	ST/Tm.
<i>D. ulicina</i> Sm.	Bb	Red	Delph. X	Mon.	ST/Tm.
<i>Desmodium latifolium</i> DC.	A	Blue	Malv.	Mon.	NG.
<i>D. polycarpum</i> DC	A	Red/Blue	Malv.	PG. + Digly.	NG.
<i>Dillwynia cinerascens</i> R.Br.	Bb	Red	Malv.	PG. ?	Tm.
<i>D. ericifolia</i> Sm.	Fruit	Red	Cyan.	PG.	ST/Tm.
<i>D. floribunda</i> Sm.	B	Red	Malv.	Dimon.	ST/Tm.
<i>D. juniperina</i> Sieb.	B	Red	Malv.	PG.	ST/Tm.
<i>Erythrina indica</i> Lam.	A*	Red	Pel.	Bios.	Tr.
<i>Glycine clandestina</i> Wendl.	A	Blue	Malv. (11)	Dimon.	G.
<i>Hovea heterophylla</i> Cunn.	A	Red/Blue	Cyan. ?	Mixture	ST/Tm.
<i>H. linearis</i> R.Br.	A	Red/Blue	Malv.	PG.	ST.
<i>H. longifolia</i> R.Br.	A	Red/Blue	Malv.	PG.	G.
<i>H. pungens</i> Benth.	A	Red/Blue	Malv.	Dimon.	WA.
			+Cyan.		
<i>H. (trisperma</i> Benth. ?)	A	Red/Blue	Malv.	Dimon.	WA
<i>Indigofera australis</i> Willd.	A	Red/Blue	Malv.	(11)	ST/Tm.
<i>Isotropis cuneifolia</i> Sm.	B	Red	Cyan.	Mon.	WA.
<i>Jacksonia scoparia</i> R.Br.	B	Red/Blue	Malv.	Mon.	ST.
<i>Kennedyia coccinea</i> Vent.	A*	Red	Peon.	Mon.	WA.
<i>K. Comptoniana</i> Benth.	A*	Red/Blue	Malv.	Dimon.	WA.
<i>K. monophylla</i> Vent.	A	Red/Blue	Malv. (11)	Dimon.	ST/Tm.
<i>K. monophylla</i> var.	A*	Red/Blue	Malv.	Dimon.	
<i>K. nigricans</i> Lindl.	A*	Red/Blue	Pet.	Dimon.	WA.
<i>K. prostrata</i> R.Br.	A	Red	Cyan.	Bios. + Mon.	ST/Tm.
<i>K. rubicunda</i> Vent.	A	Red	Peon. (11)	Mon.	G.
<i>Maniltoa grandiflora</i> Scheff.	Bracts	Pink	Cyan.	Mon.	NG.
<i>Mirbelia grandiflora</i> Ait.	Bb	Red	Malv.	Mon.-A	33/36
<i>M. reticulata</i> Sm.	A	Red/Blue	Malv.	Mon.	ST.
<i>Oxylobium callistachys</i>					
Benth.	Bb*	Red/Blue	Malv.	Mon. or PG.	WA.
<i>O. trilobatum</i> Benth.	Bb	Red/Blue	Malv.	Mon.	ST/Tm.
<i>Phyllota phyllioides</i> Benth.	Bc	Red	Malv.	PG.	ST.
<i>Platylobium formosum</i> Sm.	Bb	Red	Malv.	Mon.	ST/Tm.
<i>P. obtusangulum</i> Hk.			Malv.	Mon.	Tm.
<i>Pultenaea daphnoides</i> Wendl.	Bb	Red	Malv.	Mon.-A	Tm.
<i>P. incurvata</i> Cunn.	Bb	Red	Malv.	Mon.	33/36
<i>P. microphylla</i> Sieb.	B	Red	Pet.	PG.	ST.
<i>P. retusa</i> Sm.	B	Red	Malv. (some Fe+)	PG.	ST/Tm.
<i>P. scrabra</i> R.Br.	Fruit		Cyan.	Mon.	Tm.
<i>P. sp.</i>	B		Cyan.	PG.	
<i>Sphaerolobium vimineum</i> Sm.	B	Red	Malv.	PG.	Tm.
<i>Swainsona coronillæfolia</i>					
Salish.	A†*	Red/Blue	Delph. X (11)	Dimon.	ST.
<i>Templetonia retusa</i> R.Br.	A*	Red	Malv. (+cyan. ?)	Mon.	WA.
<i>Viminaria denudata</i> Sm.	B	Red	Cyan.	Mon.	ST/Tm.
MIMOSACEÆ (41-147).					
<i>Acacia Baileyana</i> F. Muell.	Fruit*	Red	Cyan.	Mon.	ST/Tm.
<i>A. decurrens</i> Willd. var.					
<i>normalis</i>	Fruit	Red	Delph. X	Mon. or PG.	ST/Tm.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS. —Cont.					
LEGUMINOSÆ. —Continued.					
MIMOSACEÆ. —Continued.					
<i>A. juniperina</i> Willd. ..	Fruit	Red	Malv.	PG.	ST/Tm.
<i>A. myrtifolia</i> Willd. ..	Bc	Red	Cyan. + Peon.	Mon.	ST/Tm.
<i>A. suaveolens</i> Willd. ..	Fruit	Red	Delph.	Mon.	ST/Tm.
ROSALES.					
ROSACEÆ (40–143).					
<i>Accena sanguisorbe</i> Vahl.	Ba	Red	Cyan.	Mon.	ST/Tm.
<i>Rubus parvifolius</i> Linn. ..	Fruit	Red	Cyan.	PG.	ST/Tm.
<i>R. rostrifolius</i> Sm. ..	Fruit	Red	Peon.	Mon.	G.
<i>R. sp.</i>	Fruit	Red	Pel.	PG.	NG.
CUNONIALES.					
CUNONIACEÆ (39–137).					
<i>Ceratopetalum apetalum</i>					
<i>D. Don.</i>	A†	Red	Cyan.	PG.	33/36
<i>C. gummiferum</i> Sm. ..	A	Red	Cyan.	Mon.	33/36
EUPHORBIALES.					
EUPHORBIACEÆ (38–136).					
<i>Breynia cernua</i> F. Muell.	Fruit	Red	Peon. + some Cyan.	PG.	NG.
<i>B. oblongifolia</i> F. Muell. ..	Fruit	Red	Cyan.	Bios. ?	Tr/ST.
<i>Micrantheum ericoides</i> Desf.	Bb	Red	Delph.	PG.	ST.
<i>Do.</i>	Fruit	Red	Delph.	Mon.	
<i>Phyllanthus thymoides</i> Sieb.	Fruit	Red	Delph.	PG.	ST/Tm.
<i>Ricinocarpus pinifolius</i> Desf.	Bc	Red	Delph.	PG.	ST/Tm.
MALVALES.					
MALVACEÆ (36–132).					
<i>Lagunaria Patersoni</i> Ait.	*	Pink	Malv.	Dimon.	Tr.
TILIALES.					
STERCULIACEÆ (35–130).					
<i>Abroma fastuosa</i> R.Br. ..	Bb	Red/Blue	Cyan.	Mon.	NG.
<i>Kleinhovia hospita</i> Linn.	A	Pink	Cyan.	Mon.	NG.
<i>Sterculia acerifolia</i> Cunn. ..	A*	Red	Peon.	Mon.	ST.
<i>S. discolor</i> F. Muell. ..	A*	Pink	Cyan.	Indef. (10)	ST.
<i>S. quadrifida</i> R.Br. ..	B*	Red	Cyan. + Peon.	Mon.	Tr/ST.
TILIACEÆ (35–128).					
<i>Elæocarpus obovatus</i> G. Don.					
(2)	*		Cyan.	PG.	ST.
<i>E. reticulatus</i> Sm. ..	A†	Pink	Malv.	Mon.	ST/Tm.
<i>Do.</i>	Fruit	Blue	Malv.	Mon.	
MYRTALES.					
MELASTOMACEÆ (33–120).					
<i>Melastoma malabathricum</i>					
Linn.	A†*	Blue	Indef. (12)	Digly.	Tr/ST.
LECYTHIDACEÆ (33–119).					
<i>Barringtonia (calyptrocalyx</i>					
K. Schum. ?)	A	Red	Malv. (some Fe +)	PG.	NG.
MYRTACEÆ (33–118).					
<i>Angophora cordifolia</i> Cav.	(13)	Red	Cyan.	PG.	33/36
<i>A. intermedia</i> DC. ..	(13)	Red	Delph.	PG.	ST/Tm.
<i>A. lanceolata</i> Cav. ..	(13)	Red	Delph.	PG.	ST/Tm.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
MYRTALES.—Continued.					
MYRTACEÆ.—Continued.					
<i>Callistemon acuminatus</i> Cheel	*	Red	Pet.	Mon.	
<i>C. citrinus</i> Stapf. var. <i>splendens</i>	A*	Red	Cyan. (2)	Digly.	
<i>C. hortensis</i> Hort.	*	Red	Delph.	PG.	
<i>C. lanceolatus</i> DC.	A	Red	Cyan.	Mon.	G.
<i>C. lilacina</i> Cheel	A*	Red/Blue	Indef. (12)		
<i>C. lilacina</i> var. <i>carmina</i>	A*	Red	Pet.	Mon.	
<i>C. pinifolius</i> DC.	Bc	Red	Cyan.	Mon.	33/36
<i>C. speciosus</i> DC. (3)	A*	Red	Cyan. + Delph.	Dimon.	WA.
<i>C. viminalis</i> (Sol.) Cheel.	A*	Red	Pet.	Mon.	ST.
<i>Calothamnus chrysanthus</i> F. Muell.	A*	Red	Malv.	Bios.	WA.
<i>C. quadrifidus</i> R.Br.	A*	Red	Indef. (12)	Indef. (10)	WA.
<i>C. sanguineus</i> Labill.	A*	Red	Cyan. (some Fe—)	Mon.	WA.
<i>C. villosus</i> R.Br.	A*	Red	Malv.	Mon.	WA.
<i>Chamælaucium uncinatum</i> Schau.	A†*	Pink	Malv. (some Fe+)	Dimon.	WA.
<i>Darwinia fascicularis</i> Rudge	Bracts	Red	Cyan.	Mon.	ST.
<i>Eucalyptus ficifolia</i> F. Muell.	A*	Red	Peon. ? (14)	Bios.	WA.
<i>Eugenia Smithii</i> Poir.	Fruit	Red/Blue	Malv.	Bios.	G.
<i>Kunzea capitata</i> Reichb.	A	Red/Blue	Malv.	Bios.	ST/Tm.
<i>Leptospermum citratum</i> Cheel, Challinor et Penfold	Bc*	Pink	Malv.	Mon.	
<i>L. lævigatum</i> F. Muell.	A	Pink	Delph.	Mon.	ST/Tm.
<i>L. scoparium</i> Forst.	A†*	Pink	Malv. (some Fe+)	PG.	ST/Tm.
<i>L. scoparium</i> var. <i>Nicollsi</i> (6)	A*	Red	Cyan.	Mon.	
<i>L. scoparium</i> var. <i>persiciflorum</i>	A	Pink	Malv.	PG.	
<i>Melaleuca crassifolia</i> Benth.	A*	Pink	Malv. ?	Mon. or PG.	WA.
<i>M. elliptica</i> Labill.	A*	Red	Malv. (+cyan. ?)	PG.	WA.
<i>M. ericifolia</i> Sm.	A†	Red	Delph.	PG. ?	ST/Tm.
<i>M. hypericifolia</i> Sm.	A*	Red	Delph.	A-sugar	ST/Tm.
THEALES.					
SAURALACEÆ (32–113).					
<i>Saurauia</i> sp.	Fruit	Red	Cyan.	Mixture	NG.
PASSIFLORES.					
PASSIFLORACEÆ (29–101).					
<i>Passiflora foetida</i> Linn.	Bb	Red/Blue	Malv.	Mon.	NG.
Do.	Bracts	Red	Delph.	PG.	
<i>P. Herbertiana</i> Lindl.	Bb†	Red	Peon.	PG.	G.
PITTOSPORALES.					
TREMANDRACEÆ (26–90).					
<i>Tetratheca ciliata</i> Lindl.			Indef. (12)		Tm.
<i>T. ericifolia</i> Sm.	A	Red/Blue	Malv. ? (Fe+)	Mixture	Tm.
<i>T. thymifolia</i> Sm.	A	Red/Blue	Malv.	Mixture.	ST/Tm.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
DILLENIALES.					
DILLENIACEÆ (24–85).					
<i>Hibbertia Billardieri</i> F. Muell.	Calyces		Delph.	PG.	ST/Tm.
<i>H. volubilis</i> Andr. (2) ..	Calyces*	Red	Cyan.	Mon.	Tr/ST.
PROTEALES.					
PROTACEÆ (23–84).					
<i>Banksia ericifolia</i> Linn. ..	Fruit	Red	Delph.	Mon.	ST.
<i>Conospermum ericifolium</i> Sm.	A	Red/Blue	Cyan.	Bios.	33/36
<i>C. longifolium</i> Sm. ..	A†	Red/Blue	Pet.	PG.	33/36
<i>C. tenuifolium</i> R.Br. ..	A†	Red/Blue	Delph.	Dimon.	33/36
				+ Mon.	
<i>C. sp.</i>	A	Blue	Pet.	PG.	WA.
<i>Grevillea acanthifolia</i> Cunn.	A	Red/Blue	Delph.	Bios.	33/36
<i>G. Banksii</i> R.Br. ..	A†*	Red	Cyan.	PG.	ST.
<i>G. bipinnatifida</i> R.Br. ..	A	Red	Cyan.	PG. or Mon.	WA.
<i>G. buxifolia</i> R.Br. ..	Bb	Red	Cyan.	Bios.	33/36
<i>G. Caleyi</i> R.Br. ..	A*	Red	Cyan.	Bios.	33/36
<i>G. juniperina</i> R.Br. ..	Bb†	Pink	Malv.	PG.	33/36
<i>G. lanigera</i> Cunn. ..	Bc	Red	Delph.		Tm.
<i>G. laurifolia</i> Sieb. ..	A	Red	Delph.	PG.	33/36
<i>G. linearis</i> R.Br. ..	A	Red	Cyan.	PG.	33/36
<i>G. punicea</i> R.Br. ..	A	Red	Cyan. (11)	Mon.	33/36
<i>G. robusta</i> Cunn. ..	Bb*	Red	Delph.	PG.	ST.
<i>G. sericea</i> R.Br. ..	A	Pink.	Malv.	Dimon.	33/36
<i>G. sphacelata</i> R.Br. ..	Bc	Red	Cyan.	PG.	ST/Tm.
<i>G. trinervis</i> R.Br. ..	A	Pink	Cyan.	Mixture	ST.
<i>Hakea laurina</i> R.Br. ..	B*	Pink	Cyan.	Mixture	WA.
<i>H. propinqua</i> Cunn. ..	Fruit		Delph.		33/36
<i>H. saligna</i> Knight ..	Fruit		Delph.	Mixture	ST.
<i>Lambertia formosa</i> Sm. ..	A	Red	Malv.	Mon.	33/36
<i>Persoonia linearis</i> Andr.	Fruit	Blue/Black	Malv.	PG.	ST/Tm.
<i>P. pinifolia</i> R.Br. ..	Fruit	Blue/Black	Cyan.	PG.	33/36
<i>P. myrtilloides</i> Sieb. ..	Fruit	Blue/Black	Delph.	PG.	Tm.
<i>Telopea speciosissima</i> R.Br.	A	Red	Cyan.	Mon.	33/36
THYMELÆALES.					
THYMELÆACEÆ (22–181).					
<i>Phaleria Neumannii</i> F. Muell.	Bc*		Delph. ?	Mon.	Tr.
Do.	Fruit*	Red	Delph.	Mon.	
<i>Pimelia linifolia</i> Sm. ..	Bc†	Pink	Delph.	Digly.	G.
LYTHRALES.					
HALORRHAGACEÆ (21–78).					
<i>Halorrhagis teurcroides</i> Gray	Bb	Red	Delph.	Mon.	ST/Tm.
SONNERATIACEÆ (21–74).					
<i>Sonneratia alba</i> Sm. ..	A†	Red	Cyan.	Bios. + PG. ?	NG.
GERANIALES.					
GERANIACEÆ (20–67).					
<i>Pelargonium australe</i> Willd.	A	Pink	Delph.	Dimon.	G.
LINACEÆ (20–65).					
<i>Linum marginale</i> Cunn. ..	A	Red/Blue	Delph.	Dimon.	G.
CHENOPODIALES.					
CHENOPODIACEÆ (19–61).					
<i>Atriplex cinerea</i> Poir. ..	A♂	Red	Nitrogenous		ST/Tm.
<i>Suaeda maritima</i> Dumont (3)	A†*	Red	Nitrogenous		G.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
DICOTYLEDONS.—Cont.					
POLYGONALES.					
POLYONEACEÆ (18–57).					
<i>Polygonum</i> sp.			Cyan.	PG.	
CARYOPHYLLALES.					
PORTULACACEÆ (17–56).					
<i>Portulaca oleracea</i> Linn. (5)	Stems	Red	Nitrogenous		G.
FICOIDACEÆ (17–55).					
<i>Mesembryanthemum æquilaterale</i> Haw.	A	Red/Blue	Nitrogenous +small amount of cyan.		G.
<i>Sesuvium portulacastrum</i> Linn. (5)	Bb	Pink	Nitrogenous		ST.
SARRACENIALES.					
DROSERACEÆ (15–48).					
<i>Drosera auriculata</i> Backh.	(15)	Red	Cyan.	Mixture	ST/Tm.
<i>D. binata</i> Labill.	(15)	Red	(Malv. +Cyan. ?)	Mixt.-A	ST/Tm.
<i>D. pygmæa</i> DC.	(15)	Red	Pel.	A-sugar	ST/Tm.
<i>D. spathulata</i> Labill.	(15)	Red	Pel.		G.
SAXIFRAGALES.					
SAXIFRAGACEÆ (14–47).					
<i>Bauera rubioides</i> Andr.	A†	Pink	Indef. (12)	PG.	ST/Tm.
POLYGALES.					
POLYGALEACEÆ (13–42).					
<i>Bredemeyera volubile</i> Steetz		Red/Blue	Delph.	Bios.	ST/Tm.
<i>Comesperma ericinum</i> DC.	A	Red/Blue	Cyan.	Bios.	ST/Tm.
<i>Polygala paniculata</i> Linn. var. <i>canchalagha</i>	Bracts	Blue	Cyan.	Dimon.	NG.
VIOLALES.					
VIOLACEÆ (12–40).					
<i>Hybanthus filiformis</i> F. Muell.	A	Blue	Delph.	Dimon.	ST/Tm.
<i>Viola betonicifolia</i> Sm.	A	Red/Blue	Malv. X	Dimon.	ST/Tm.
<i>V. hederacea</i> Labill.	A†	Red/Blue	Delph.	Dimon.	ST/Tm.
<i>V. hederacea</i> var.	A	Red/Blue	Delph.	Dimon.	
LAURALES.					
LAURACEÆ (3–11).					
<i>Cryptocarya glaucescens</i> R.Br.	Fruit	Blue/Black	Cyan.	Mixture	Tr/ST.
MONIMIACEÆ (3–10).					
<i>Doryphora Sassafras</i> Endl. (2)	†*		Cyan.	PG.	ST.
MAGNOLIALES.					
WINTERACEÆ (1–2).					
<i>Drimys dipetala</i> F. Muell.	Fruit	Red	Cyan.	Mixture	ST.
MONOCOTYLEDONS.					
GRAMINALES.					
GRAMINEÆ (105–332).					
<i>Brachiaria reptans</i> Gard. et C.E.H.	Fruit	Red	Cyan.	Mon.	NG.
<i>Pennisetum macrostachyum</i> Trin.	Bc	Red	Malv.	Mon.	NG.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
MONOCOTYLEDONS.— <i>Continued.</i>					
GRAMINALES.—Continued.					
GRAMINEÆ.—Continued.					
<i>Saccharum spontaneum</i> Linn.	Fruit	Red	Cyan.	Mon.	NG.
<i>Spinifex hirsutus</i> Labill. . .	Bracts	Red	Malv.	PG. or Mon.	G.
<i>Themeda Forskalii</i> Hack.		Red	Delph. ?	PG.	
JUNCALES.					
RESTIONACEÆ (103-330).					
<i>Leptocarpus tenax</i> R.Br. . .	Bracts	Red	Malv.	Mon. or PG.	Tm.
ORCHIDALES.					
ORCHIDACEÆ (103-236).					
<i>Acianthus fornicatus</i> R.Br.	Bb	Red/Blue	Cyan.	Bios.	ST.
<i>Caladenia carnea</i> R.Br. . .	Ba†	Pink	Cyan. + some Malv.	Bios.	ST/Tm.
<i>C. Patersoni</i> R.Br. . .	Bb	Red/Blue	Malv. (trace Fe+)	Bios.	ST/Tm.
<i>Caleana major</i> R.Br. . .	A	Red	Cyan.	A-sugar	ST/Tm.
<i>Dipodium punctatum</i> R.Br.	A	Red/Blue	Cyan.	A-sugar	G.
<i>Diuris aurea</i> Sm. . .	Bb	Red	Cyan.	Dimon.	ST.
<i>D. elongata</i> Swartz. . .	A	Red/Blue	Malv.	Bios.	ST/Tm.
<i>D. sulphurea</i> R.Br. . .	Bb	Red/Blue	Malv. (Fe+)	Dimon.	ST/Tm.
<i>Glossodia major</i> R.Br. . .	A†	Red/Blue	Delph.	Dimon. (11)	ST/Tm.
<i>G. minor</i> R.Br. . .	A†	Blue	Pet.	Dimon.	ST/Tm.
<i>Prasophyllum (elatum</i> <i>R.Br. ?)</i> . . .	Ba	Red/Blue	Cyan.	Dimon.	Tm.
<i>Thelymitra ixoides</i> Swartz. .	A	Blue	Cyan.	Dimon.	ST/Tm.
<i>T. venosa</i> R.Br. . .	A	Blue	Cyan.	Mon.	Tm.
HÆMODORALES.					
HÆMODORACEÆ (100-317).					
<i>Anigozanthos flavida</i> Red.	Bb†*	Red	Cyan.	PG.	WA.
<i>A. Manglesii</i> D. Don. . .	Bb†	Red	Cyan.	Indef. (10)	WA.
PALMALES.					
PALMÆ (97-314).					
<i>Livistona australis</i> Mart. . .	Fruit	Blue/Black	Cyan.	Mon. + Digly.	ST.
AGAVALES.					
AGAVACEÆ (96-313).					
<i>Cordyline stricta</i> Endl. . .	A*	Red/Blue	Malv. (Fe+)	PG. + Digly.	ST.
<i>C. sp.</i> . . .	Fruit	Red	Pel.	PG.	NG.
<i>Doryanthes excelsa</i> Corr. . .	A	Red	Cyan.	Mon.	ST.
<i>D. Larkini</i> C. Moore . . .	A*	Red	Cyan.	Mixture	ST.
<i>D. Palmeri</i> Hill . . .	A*	Red	Cyan.	(11)	ST.
Do. . . .	Fruit*	Red	Cyan.	PG.	
XANTHORRHACEÆ (96-312).					
<i>Xerotes longifolia</i> R.Br. . .	Fruit		Malv.	PG.	G.
IRIDALES.					
IRIDACEÆ (94-307).					
<i>Patersonia glabrata</i> R.Br.	A	Blue	Malv.	Dimon.	ST/Tm.
<i>P. glauca</i> R.Br. . .	A	Blue	Malv.	Dimon.	ST/Tm.
<i>P. sericia</i> R.Br. . .	A	Blue	Malv.	Dimon.	ST/Tm.
ARALES.					
ARACEÆ (91-302).					
<i>Alocasia</i> sp. . . .	A	Red	Cyan. + Delph.	PG.	NG.
<i>Gymnostachys anceps</i> R.Br.	Fruit	Blue/Black	Cyan.	Mixture	Tr/ST.

TABLE 1.—Continued.

Anthocyanins Occurring in Flowers and Fruits of Native Australian Species.—Continued.

	(i)	(ii)	(iii)	(iv)	(v)
MONOCOTYLEDONS.— <i>Continued.</i>					
ALSTROEMERIALES.					
PHILESIACEÆ (90–301).					
<i>Eustrephus Brownii</i> F. Muell.	A	Red/Blue	Malv.	Bios.	G.
LILIALES.					
SMILACEÆ (89–297).					
<i>Smilax glycyphylla</i> Sm. . .	Fruit	Blue/Black	Cyan.	Mon.	Tr/ST.
<i>S. (timorensis</i> DC. ?) (16)	Fruit	Red	Peon.	Bios.	NG.
Do.	Fruit	Blue	Cyan.	Bios.	
LILIACEÆ (89–293).					
<i>Arthropodium</i> sp.	A	Red/Blue	Cyan.	PG.	
<i>Blandfordia flammea</i> Hook.	Ba	Red	Cyan.	Bios.	ST.
<i>B. grandiflora</i> R.Br. . . .	Ba*	Red	Cyan.	Bios.	ST.
<i>B. nobilis</i> Sm.	Ba	Red	Cyan.	+ Mon. Bios.	33/36
<i>Burchardia umbellata</i> R.Br.	Bb	Red	Cyan.	Bios.	ST/Tm.
<i>Cæsia vittata</i> R.Br. . . .	Bb†	Blue	Delph.	Bios.	ST/Tm.
<i>Dianella cærulea</i> Sims . .	A	Blue	Delph.	Bios.	Tr/ST.
Do.	Fruit	Blue	Delph.	Bios.	
<i>D. sp.</i>	Fruit	Blue	Delph.	Bios.	
<i>Sowerbaea juncea</i> Sm. . .	A	Red/Blue	Delph.	Dimon.	ST/Tm.
<i>Stypandra glauca</i> R.Br. . .	A	Blue	Delph.	Bios.	ST/Tm.
<i>S. sp.</i>	A	Blue	Delph.	Bios.	
<i>Thysanotus junceus</i> R.Br.	A	Red/Blue	Delph.	Bios.	ST.
<i>Wurmbea dioica</i> F. Muell.	Bb†	Red/Blue	Cyan. + Peon.	Dimon.	ST/Tm.
ZINGIBERALES.					
ZINGIBERACEÆ (88–290).					
<i>Costus (speciosus</i> Sm. ?) . .	A	Red	Cyan.	Mon.	NG.
<i>Curcuma longa</i> Linn. . . .	A	Red	Cyan.	PG.	NG.
MUSACEÆ (88–287).					
<i>Musa</i> sp.	Bracts	Red	Cyan. + Malv.	Mon.	NG.
COMMELINALES.					
COMMELINACEÆ (84–280).					
<i>Commelina cyanea</i> R.Br.	A	Blue	Delph.	PG.	Tr/ST.
JUNCAGINALES.					
JUNCAGINACEÆ (80–271).					
<i>Triglochin procera</i> R.Br.	Bc		Malv. (Fe +)	Dimon.	G.

Notes to Table 1.

The figures quoted alongside the names of the families are those allotted by Hutchinson in his classification. The first figure indicates the order, and the second the family.

(i) *Mode of Occurrence.*

* Collected from cultivated plants.

† The anthocyanin is often absent from the flowers. (It is well known that practically all species which have flowers coloured by anthocyanins occasionally appear with the anthocyanin absent.) A separate analysis indicates that the distribution of anthocyanins is much the same in these species as in normal species.

A Flowers completely or mostly coloured by anthocyanin. Other pigments, if present, completely or largely masked by the anthocyanin.

B Flowers coloured by anthocyanin together with large amounts of other pigments (carotenoids, yellow and white anthoxanthins, chlorophyll, etc.).

Ba—Anthocyanin colouring most of the flower.

Bb—Anthocyanin colouring only a small amount of the flower (often as spots or streaks on the petals).

Bc—Anthocyanin in very small amount (often colouring a minor part of the flower).

(ii) *Colour of Anthocyanin.* (Not necessarily always the colour of the whole flower.)

Red Includes all shades of red—orange red, scarlet, crimson, etc.—excluding pink and shades with a bluish tinge.

Red/Blue Ranges from red with a bluish tinge to blue with a reddish tinge. Includes mauve, lilac, violet, etc. Also includes flowers with separate areas of red and blue. Generally well on the blue side.

Blue No reddish tinge.

(iii) *Anthocyanidin.*

Malv. X Malvidin + delphinidin and/or petunidin.

Delph. X Delphinidin + malvidin (+ petunidin ?).

Malv. Fe + Malvidin giving positive ferric test due to admixture with delphinidin (and/or petunidin) or cyanidin.

(iv) *Glycoside Type.* The nomenclature is that used in previous surveys except that the enumeration is omitted, it being understood that the sugars are attached in the usual positions.

Mixt. Mixture of diglycoside and monoglycoside.

Digly. Dimonoside or bioside.

A Acylated.

A-sugar The sugar is attached to an acyl group which is attached to the anthocyanidin.

(v) *Distribution.*

NG. Species collected in New Guinea (Huon Gulf district. Latitude 7° S.). Many of these extend into north Queensland.

WA. Species native to Western Australia and not occurring in eastern Australia. Almost all the species listed are restricted to the south-western corner. (Latitude from approx. 28° S. to 35° S.).

The remainder of the species examined are from eastern Australia and are almost all native to the coastal and dividing range section though many extend inland as well. For the purpose of analysis of the results they have been divided into the following geographical subdivisions based on the distributions given for each species in the Floras of the various States.

Tr. Tropical. Species growing mainly or entirely in central and north Queensland (down to Lat. 24° S.).

ST. Sub-tropical. Species growing in south Queensland and northern N.S.W. Approximately between latitudes 24° S. and 32° S.

33°/36° Species whose habitat appears to be restricted to this range of latitude. (The comparatively large number of such species is due to the fact that a large number of the plants examined were collected in this area.)

ST/Tm. Sub-tropical to temperate. Species whose habitat extends from south Queensland into Victoria or Tasmania. (South of Lat. 26° S.)

Tm. Temperate. Species extending from southern N.S.W. into Victoria and Tasmania (South of Lat. 36° S.)

G. General distribution. Species extending from north or central Queensland into Victoria and Tasmania and westwards. (Victorian species were collected while one of us (D.E.W.) was at the Chemistry Department of the University of Melbourne.)

Miscellaneous.

1 Lawrence *et al.*, 1938.

2 Price and Sturgess, 1938.

3 Lawrence *et al.*, 1939.

4 Cornforth, 1939.

5 Taylor, 1940.

6 Beale *et al.*, 1941.

7 The material was very readily extracted by 1% hydrochloric acid yielding a solution of the normal red colour which turned black in 24 hours.

- 8 The extract gave the tests for a bioside but the pigment was destroyed by acid hydrolysis.
- 9 The dark red extract gave the distributions of a pentoseglycoside but was not hydrolysed by boiling with 15% hydrochloric acid for 15 minutes. Apparently a non-anthocyanin water-soluble pigment.
- 10 The extract contained a pigment with a much higher distribution to amyl alcohol than a monoside but was unaffected by alkaline hydrolysis. Probably due to enzymatic hydrolysis.
- 11 See Table 2.
- 12 Probably a normal anthocyanidin but no definite results could be obtained due to persistent contamination by other substances in the extract. The ferric test appeared negative but was obscured by the presence of tannins, distribution to the cyanidin reagent was zero and to the delphinidin reagent very low, or in most cases, zero. The colour in amyl alcohol at neutrality was generally very much on the red side and the pigment was not destroyed in the oxidation test. These effects were also observed with extracts in which the anthocyanin content was very low.
- 13 Dark red hairs on the inflorescence (the flowers are white).
- 14 From a cultivated tree probably a hybrid with *E. calophylla*, a white flowered species. (The *Eucalyptus* genus forms a large part of the vegetation of Australia but very few of the species have anthocyanin-coloured flowers.)
- 15 Red insectivorous hairs on the leaves. The flowers are white or pink.
- 16 The fruit was a berry with a red skin and had at the centre a rubbery sac containing the seeds embedded in a paste of semi-solid blue anthocyanin. The red pigment of the skins was found to be peonidin bioside and the blue pigment cyanidin bioside.

CONSTANCY OF SPECIFIC PIGMENTATION.

In any survey of anthocyanins the tacit assumption is made that the anthocyanin pigmentation of a species is constant irrespective of locality and environment. This cannot always be the case, particularly in variable species and species which have a wide distribution.

In a number of cases we have determined the anthocyanins in two lots of material of the same species which were collected in localities at least 500 miles apart. In some cases also we have re-examined Australian species which were included in previous surveys and which we assume were collected from cultivated plants. The results are summarised in Table 2, and it will be seen that there is considerable variation in the sugar residues. In some cases this may be more apparent than real because of interference by impurities in the plant extracts with the tests for glycoside type. This applies particularly to the distinction between dimonosides and biosides. Also Lawrence *et al.* (1939) have pointed out that impurities may cause a monoside to behave like a pentoseglycoside. However, the distinction between a dimonoside or bioside on the one hand and a monoside or pentoseglycoside on the other is unmistakable.

TABLE 2.

Comparison of Anthocyanin Content of a Species Collected in Two Distant Localities.

(a) Wild Material Only.

Platylobium formosum: Malvidin monoside in two lots of material.

Glossodia major: Delphinidin dimonoside in material from N.S.W. Delphinidin bioside in material from Victoria.

Chianthus Dampieri: Material from both Western Australia and central Australia had pelargonidin monoside in the red petals and cyanidin monoside in the black spot on the standard petals. Lawrence *et al.* (1939) also record pelargonidin monoside with a little cyanidin. The species occasionally varies somewhat in colour.

Indigofera australis: Malvidin monoside+dimonoside in material from N.S.W. Malvidin bioside in material from Victoria (both wild and cultivated).

Glycine clandestina: Malvidin monoside in material from N.S.W. Ferric-positive malvidin bioside in material from Victoria.

(b) Wild and Cultivated Material.

Epacris longiflora: Cyanidin monoside in both lots of material.

Prostanthera ovalifolia: Partially methylated delphinidin dimonoside in wild material from N.S.W. Partially methylated delphinidin bioside in cultivated material from Victoria.

Grevillea punicea: Cyanidin monoside in wild material. Lawrence *et al.* (1939) found cyanidin pentoseglycoside.

Convolvulus sepium: Cyanidin dimonoside in wild material. Lawrence *et al.* (1939) found cyanidin monoside. It is to be noted that wild material of *C. sepium* var. *Soldanella* contains cyanidin monoside.

Helipterum Manglesii: Peonidin bioside in wild material. Lawrence *et al.* (1939) found cyanidin dimonoside.

Kennedya coccinea: Peonidin monoside in both lots of material.

K. rubicunda: Peonidin monoside in wild material. Beale *et al.* (1941) found pelargonidin monoside. This difference may not be real and may be due to the difficulty of distinguishing between pelargonidin and peonidin (p. 62).

K. monophylla: Two wild specimens collected in N.S.W. and Victoria and also a cultivated variety all contained malvidin dimonoside. A cultivated form which appeared rather different morphologically contained ferric-positive malvidin dimonoside.

(c) Cultivated Material Only.

Graptophyllum Earlii: Pelargonidin monoside in two lots of material.

Eugenia Smithii (fruit): Malvidin bioside in two lots of material.

Callistemon viminalis: Petunidin monoside in two lots of material.

Sterculia ucerifolia: Peonidin monoside in two lots of material.

Doryanthes Palmeri: Cyanidin pentoseglycoside in both the flowers and fruit of material cultivated in N.S.W. Cyanidin monoside in material cultivated in Victoria.

Boronia megastima: Partially methylated delphinidin pentoseglycoside with some bioside in material cultivated in N.S.W. Delphinidin bioside in material cultivated in Victoria. (This species is extensively cultivated.)

Swainsona coronillæfolia: The flower coloration of this species is very variable even in the wild. A red form contained a mixture of delphinidin and malvidin dimonoside and a light blue form contained malvidin dimonoside. Beale *et al.* (1941) found delphinidin dimonoside.

In the twenty species examined there are only five, excluding the doubtful case of *Kennedya rubicunda*, in which the anthocyanidin varies with locality or cultivation and in these the variation is only in the degree of methylation and in most cases is slight. On the other hand there is considerable variation in the sugars which is not all due to difficulties of identification.

CORRELATION OF ANTHOCYANIN WITH FLOWER COLOUR.

It is well known that the colour of a flower is determined not only by the anthocyanin that it contains but also by other factors, in particular the pH of the cell sap and copigmentation of the anthocyanin with tannins or white anthoxanthins. Blueing of flower colours, i.e. shifting of the colour towards blue, is caused by copigmentation and also by decreased acidity of the cell saps, which are invariably slightly acidic (Scott-Moncrieff, 1939).

Table 3 shows the numbers of the various types of anthocyanins which were found in flowers of four colour groups, and the proportions are represented graphically in Figure 1. In discussing these results it is assumed that copigmentation is the major factor causing blueing of flower colour. Differences in cell sap pH have not been considered, and may be of only minor importance in wild species since natural selection favours comparatively strongly acid cell sap (Beale, 1941).

The results indicate two trends. Firstly the occurrence of copigmentation increases with the number of sugar and phenolic hydroxyl groups, and to a less extent methoxyl groups, in the anthocyanin molecule. Thus copigmentation

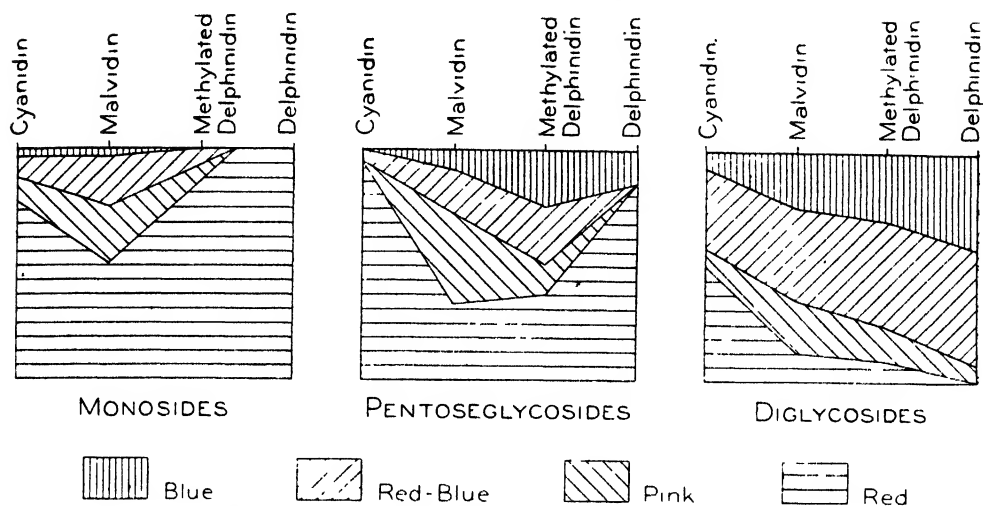


Fig. 1.—Relation between Anthocyanin and Colour.
(Numbers in Table 3 which are too small to have much significance have been excluded.)

TABLE 3.
Relation between Anthocyanin and Flower Colour.

					Red.	Pink.	Red/Blue.	Blue.
Pelargonidin	Diglycosides	2	—	—	—
	Pentoseglycosides	—	—	—	—
	Monosides	2	—	—	—
	Total	6	—	—	—
Peonidin and Peonidin + Cyanidin	Diglycosides	1	1	2	—
	Pentoseglycosides	3	—	—	—
	Monosides	8	—	—	—
	Total	13	1	3	—
Cyanidin	Diglycosides	12	2	8	2
	Pentoseglycosides	16	—	1	—
	Monosides	30	4	4	1
	Total	64	9	14	3
Malvidin	Diglycosides	4	7	12	8
	Pentoseglycosides	4	4	3	1
	Monosides	12	6	5	1
	Total	23	18	25	11
Petunidin and Methylated Delphinidin Mixtures	Diglycosides	1	2	6	4
	Pentoseglycosides	3	1	2	2
	Monosides	5	—	—	—
	Total	10	3	8	8
Delphinidin	Diglycosides	—	2	13	11
	Pentoseglycosides	12	—	—	2
	Monosides	4	1	—	—
	Total	20	3	14	15

Notes to Table 3.

The colour groups are as already defined in the notes to Table 1.

"Diglycoside" includes both 3,5-dimonosides and 3-biosides since these both show the same trends.

"Total" includes in addition to the normal sugar types acylated anthocyanins, mixtures of sugars and indefinite sugars.

The cultivated Australian species have been included.

Species in which the anthocyanin pigmentation is subsidiary to other types of pigments (Class B of Table 1) have been included since a separate analysis indicated that the relationships between anthocyanin and flower colour in these species is virtually the same as in species with flowers entirely pigmented by anthocyanin (Class A).

is much more common in diglycosides than in monosides, pentoseglycosides* being intermediate, and also increases rapidly from pelargonidin and peonidin through cyanidin to malvidin and delphinidin. This effect has been previously recognized (Scott-Moncrieff, 1939). Superimposed on this trend is a second one. The frequency of copigmentation of malvidin, and to a less extent of methylated delphinidin mixtures, relative to that of delphinidin is high in monosides but decreases through pentoseglycosides to diglycosides. This affect applies particularly to the less intense copigmentations, i.e. pink and red/blue, and may be due to a low occurrence of copigmented delphinidin monosides and pentoseglycosides or, more likely, to a high occurrence of copigmented malvidin glycosides.

Whilst the first of these trends appears explicable on physico-chemical lines, the second may be due to genetic factors. Beale, Robinson, Robinson and Scott-Moncrieff (1939) observed that there appears to be a correlation between methylation and copigmentation and that pure methylated types tend to occur with high copigment. Lawrence *et al.* (1939) noted that copigments have a greater effect on malvin than on petunin.

Robinson (1933, 1942) considers that blue pigmentation by an anthocyanin in an acidic cell sap is made possible by the occurrence of the anthocyanin in colloidal solution in the sap, and that the attainment of the colloidal state is aided by the presence of copigments and possibly by protective colloids. On this view the dependence of copigmentation on the number of hydroxyl groups in the anthocyanin molecule can be considered due to the hydroxyl groups effecting association between the molecules and uniting a number of them together to form a colloidal particle, presumably by such mechanisms as hydrogen bonding, dipole association and salt formation. In this connection it may be observed that the tannin and anthoxanthin copigments are themselves polyhydroxy compounds. It appears that seven hydroxyl groups in an anthocyanin molecule (pelargonidin and peonidin monoglycosides) are insufficient to cause any appreciable degree of association or copigmentation, but when the number rises to twelve (delphinidin diglycosides) association is readily effected.

DISTRIBUTION OF THE ANTHOCYANIDIN TYPES.

The data of Table 3 may be condensed to show the proportions of the three anthocyanidin types occurring in flowers of different colours (Table 4). Whilst it cannot be assumed that these proportions, found in Australian flowers, will be the same in flowers of all localities, there is little doubt that the trends illustrated are universal. Thus nearly all blue flowers will contain delphinidin type, the majority of red flowers will contain cyanidin type and the occurrence of pelargonidin will be almost entirely restricted to red flowers. It is apparent therefore

TABLE 4.
Relative Occurrence of the Anthocyanidin Types in Flower Pigmentation.

Colour of Anthocyanin in Flower.	Number of Species.	Pelargonidin %	Cyanidin %	Delphinidin %
Red	134	4.5	57	38
Pink	34	—	26	74
Red/Blue	65	—	29	71
Blue	38	—	10	90

* As in previous surveys, the term pentoseglycoside indicates a disaccharide sugar residue consisting of a hexose and a pentose.

that the proportion of the three anthocyanidin types found in any survey will be determined by the proportion of red to blue flowers—the “colour ratio”—in the species examined. Table 4 shows general trends only and certain families, e.g. *Myrtaceæ*, may be conspicuous exceptions.

It is possible for the colour ratio, and consequently the distribution of the anthocyanidin types, in a group of cultivated species to differ considerably from the natural colour ratio in wild species. (Variation of the colour ratio in wild species with climate is discussed below.) This position is illustrated by a comparison of the wild and cultivated Australian species collected (Table 5). In this case the preference for red in the artificial selection of the cultivated flowers is very marked, probably because most of the red flowers were large and striking (e.g. *Myrtaceæ*), and for other horticultural reasons.

TABLE 5.
Colours of Species Collected.

	Red.	Pink.	Red/Blue.	Blue.
Wild (219 spp.)	43%	13%	26%	17%
Cultivated (56 spp.)	65%	16%	14%	5%

TABLE 6.
Distribution of Anthocyanidins in the Flowers of Australian Wild Species.

	Total Number Examined.	Pelargonidin %	Cyanidin. %	Delphinidin %
Species.	228	1.7	41	62.5
Genera	133	2	47	63
Families	54	5.5	54	78
Orders	41	7	66	83

Notes.

The cultivated Australian species are not included. The New Guinea species are included but approximately 90% of the total number of species are extra-tropical.

TABLE 7.
Distribution of Anthocyanidins in Flowers as Found in Previous Surveys.
(Beale *et al.*, 1941.)

	Total Number Examined.	Pelargonidin %	Cyanidin %	Delphinidin %
Species.	530	19	40	50
Genera	299	23	52	49.5
Families	88	37.5	73	65
Orders	54	44	80	72

Comparison of the distribution of the anthocyanidin types in the Australian wild species (Table 6) with the results of previous surveys (Table 7) shows considerable differences, in particular the more limited occurrence of pelargonidin

and the appearance of delphinidin rather than cyanidin as the most widespread anthocyanidin type in the Australian species. These differences might at first sight be considered due to different colour ratios in the two lots of material in which case a high proportion of red in the flowers examined in previous surveys would be inferred. However, this inference is directly opposed to that which may be drawn from comparison of glycoside distributions (p. 65) and degrees of methylation (p. 63).

On the other hand the differences between the two surveys are in accordance with recent genetical findings. Beale (1941) deduced that when an anthocyanin-containing wild type mutates, the direction of mutation is predominantly from delphinidin to cyanidin or pelargonidin, and from cyanidin to pelargonidin, that is from the more to the less oxidised anthocyanidin. Also, mutant types were found to be recessive. In cultivated plants the mutants have a much greater chance of survival, due to artificial selection and breeding of new types, than they have in the wild, where they are usually less viable than the normal types. It follows that cultivation should increase the occurrence of pelargonidin and cyanidin at the expense of delphinidin. Comparison of Tables 6 and 7 indicates that this is the case.

In ascribing to the effects of mutation and artificial selection the differences between the two surveys the assumption is of course made that were it not for this factor the Australian flora examined would be comparable in respect to anthocyanin distribution with the flora examined in the previous surveys. To what extent this assumption is justifiable is not certain in view of the special nature of the Australian flora, which is generally regarded as having been evolved in an intense struggle for existence with consequent great importance of floral pigmentation. It may be noted, however, that the group of families examined in each of the two surveys is much the same.

In the case of pelargonidin the difference between the two sets of figures in Tables 6 and 7 is very striking. Moreover of the six species found to contain pelargonidin (four in the wild and two in the Australian cultivated flowers) most were tropical or sub-tropical species. Thus pelargonidin is a very rare anthocyanidin in temperate Australian plants. The much more frequent occurrence in garden flowers is no doubt due to the fact that it can arise by mutation from both of the other anthocyanidin types, and may also be due to preference for red and orange-red shades. Lawrence *et al.* (1939) noted that many of the flowers which they found to contain pelargonidin originated from tropical or sub-tropical countries. We have found that although the proportion of pelargonidin is higher in tropical and sub-tropical flowers than in temperate flowers (Table 11) it is still very low.

The occurrence of pelargonidin recorded may possibly be slightly less than is actually the case since the distinction between pelargonidin and peonidin in the identification of anthocyanidins is not very definite. However, peonidin is well differentiated from the rest of the anthocyanidins and only eight occurrences of peonidin (not mixed with cyanidin) were found in the wild species and three in the cultivated species. Some of these may have actually been pelargonidin, but even if they are all counted as pelargonidin its occurrence in the wild species rises to only 5%.

A graphical representation (Figure 2) of the figures of Tables 6 and 7 reveals three points of interest: the predominance of delphinidin in the wild flowers, the similarity in shape of the two delphinidin graphs, and the comparative steepness of the cyanidin graph in the garden flowers. Such graphs are not likely to be greatly modified if a larger number of species is examined.

The approximate equivalence of the proportions of delphinidin-containing genera and species in the two delphinidin graphs appears significant. Lawrence

et al. (1939) considered that this effect was artificial and due to preference for the extremes of colour in artificial selection. This cannot be the case, for the effect appears in the wild flowers.

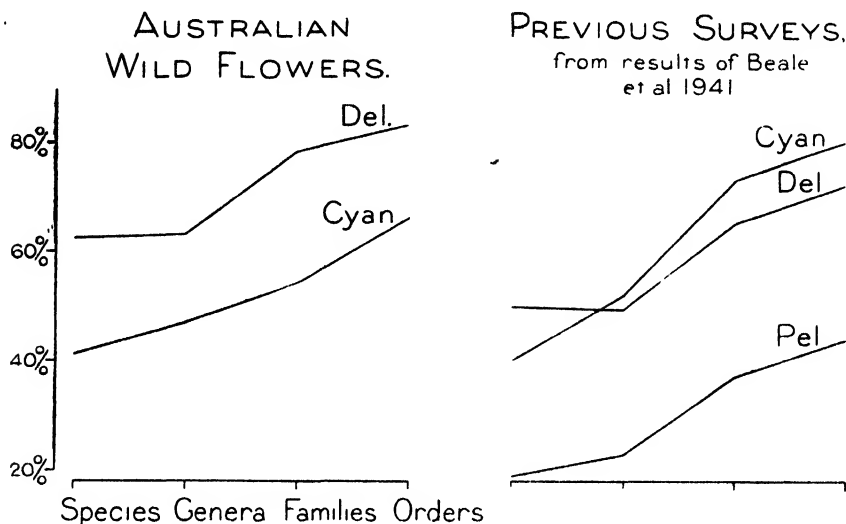


Fig. 2.—Distribution of Anthocyanidin Types.

METHYLATION.

The degree of methylation of cyanidin or delphinidin may be defined as the ratio of the number of occurrences of methyl derivatives (including mixtures due to incomplete methylation) of cyanidin or delphinidin to the total number of occurrences of cyanidin or delphinidin type. In Table 8 the degree of methylation of cyanidin and delphinidin in the previous surveys and the Australian wild species is compared. The term "methylated delphinidin" is used to denote mixtures of the methyl derivatives of delphinidin, or partially methylated

TABLE 8.
Degree of Methylation.

	Australian Wild Flowers (228 spp.).		Previous Surveys* (382 spp.).	
	Number.	%	Number.	%
Peonidin	8	3.5	7	2
Peonidin + cyanidin	5	2	—	—
Cyanidin	80	35	139	36
Degree of methylation of cyanidin	13/93	14	7/146	5
Malvidin	66	29	74	19
Methylated delphinidin	23	10	7	2
Petunidin	4	2	10	2.5
Delphinidin	49	21.5	109	28.5
Degree of methylation of delphinidin	93/142	65.5	91/200	45.5

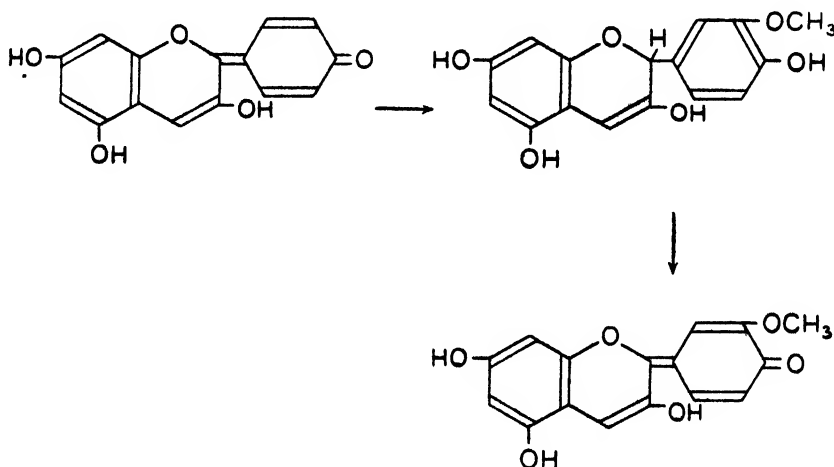
* Figures taken from the results of Lawrence *et al.* (1939).

delphinidin. Ferric positive malvidin has also been included under this heading since there seems little doubt that in the great majority of cases the positive ferric test is due to the presence of small amounts of delphinidin and (or) petunidin though there is the possibility that in some cases it may be due to cyanidin.

The higher degree of methylation in the wild species suggests that cultivation preserves mutations from methylated to unmethylated types. It has already been shown that methylation varies somewhat with locality and cultivation (Table 2). On the other hand the difference in the figures might be considered due to different colour ratios in the two lots of flowers examined. However, it should be noted that in the cultivated Australian flowers (Table 9) the degree of methylation of delphinidin (85%) is even higher than in the wild flowers. This is due to the much higher proportion of red colorations in the cultivated flowers, which results in a decreased proportion of unmethylated delphinidin. It appears therefore that the results of previous surveys, showing a lower degree of methylation of delphinidin than in the wild flowers, do not reflect any undue predominance of red colorations (cf. p. 62).

Little is known of the factors controlling the formation of methylated anthocyanins. It has previously been assumed (Lawrence *et al.*, 1939) that methylation simply involves one additional stage, not necessarily the last stage, in the synthesis of the anthocyanin. The occurrence of mixtures due to partial methylation of cyanidin and delphinidin supports this view. An excellent example is afforded by the fruit of *Smilax timorensis*, which at its centre contains a paste of cyanidin bioside, but in which the skin is pigmented by peonidin bioside.

However, it seems possible that another way in which methylated derivatives may arise is by the addition of methyl alcohol to the quinonoid colour base form of the anthocyanin, followed by oxidation. For example, pelargonidin would yield peonidin. Whilst no direct evidence can be adduced in support of such a process, it may be pointed out that methylation of the 4'-hydroxyl group does not occur.



CULTIVATED SPECIES.

The results for the cultivated flowers of 56 Australian species are listed in Table 9. A number of Australian species which were examined in previous surveys have been included. Compared with the results for the wild flowers, the cultivated flowers show an increase in the proportion of cyanidin and pelargonidin at the expense of delphinidin, and also an increase in the degree of

methylation of delphinidin. These increases result from the artificially large ratio of red to blue flowers discussed above (p. 61). It is considered that the anthocyanin content of these species (most of which were collected from Botanical Gardens) has been very little affected by the preservation of mutants in horticulture since they have been cultivated for a shorter period and on a smaller scale than plants in most other countries.

TABLE 9.
Distribution of Anthocyanidins in Cultivated Australian Flowers.

	Number.	%		Number.	%
Pelargonidin	2	3.5	Pelargonidin Type ..	2	3.5
Peonidin	3	5.5			
Peonidin + cyanidin ..	1	2			
Cyanidin	25	45	Cyanidin Type	29	52
Malvidin	13	23			
Methylated delphinidin ..	6	11			
Petunidin	4	7			
Delphinidin	4	7	Delphinidin Type ..	27	48

Degree of methylation of cyanidin = $4/29=14\%$

Degree of methylation of delphinidin = $23/27=85\%$

DISTRIBUTION OF GLYCOSIDE TYPES.

In view of the relationships between anthocyanin and flower colour illustrated in Figure 1 it is to be expected that the distribution of glycoside types, like the distribution of anthocyanidins, will be largely dictated by the biological value of the flower colorations.

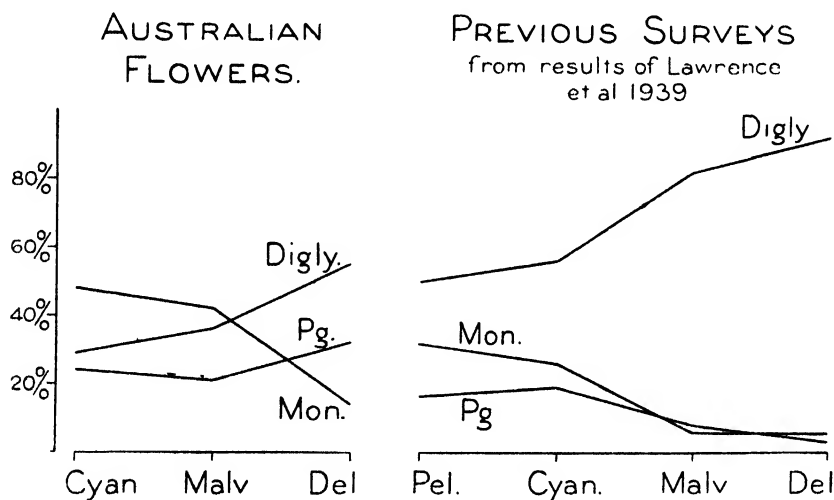


Fig. 3.—Distribution of Glycoside Types.

Comparison between the two sets of results in Table 10 and Figure 3 shows a much lower proportion of diglycosides in the Australian species. As in the case of the anthocyanidins the reasons for this difference might be either mutation, operating in the sense monoside wild type \rightarrow diglycoside mutant, or different colour ratios in the two sets of material. If the latter were the case the high proportion of diglycosides in the results of Lawrence *et al.* would indicate a

much higher proportion of blue colorations in the material examined by them than in the Australian species. (It may be taken that the relations between anthocyanin and flower coloration illustrated in Figure 1 hold also in general for cultivated flowers.) However this is directly opposed to the inference drawn from a comparison of the distribution of the anthocyanidin types (p. 62). It

TABLE 10.
Distribution of Glycoside Types.
(a) Australian Species.

	Cyanidin (86 spp.). %	Malvidin (76 spp.). %	Delphinidin (44 spp.). %
3,5-Dimonosides	10	24	34
3-Biosides	16	9	18
Total Diglycosides	29	37	55
3-Pentoseglycosides	24	21	32
3-Monosides	48	42	14

(b) Previous Surveys. (From data of Lawrence *et al.*, 1939.)

	Pelargonidin (71 spp.). %	Cyanidin (139 spp.). %	Malvidin (74 spp.). %	Delphinidin (109 spp.). %
3,5-Dimonosides	30	34		
3-Biosides	20	14	Mostly 3,5-dimonosides	
Total Diglycosides	51	56	82	92
3-Pentoseglycosides	17	19	8	3
3-Monosides	32	26	7	5.5

Notes.

The term "diglycoside" includes both 3,5-dimonosides and 3-biosides.

The Australian cultivated species are included. These have the effect of slightly increasing the predominance of monoglycosides due to the high proportion of red colorations.

Mixtures of sugars and indefinite glycoside types are excluded.

The figures include acylated glycosides of the type anthocyanidin-sugar-acyl group but not those of the type anthocyanidin-acyl group-sugar since in the latter case the glycoside type is not determined.

seems, therefore, that the differences between the two surveys in respect to the distribution of anthocyanidin and glycoside types and also degree of methylation cannot be due to any differences in the colour ratios of the two lots of material.

The genetics of factors controlling glycoside differences is at present not known with any certainty (Beale, 1941).

VARIATION OF ANTHOCYANIDIN TYPE WITH CLIMATE.

It was observed by Lawrence *et al.* (1939) that many of the flowers which they found to contain pelargonidin originated from tropical or sub-tropical countries. These authors also suggested that delphinidin appeared to predominate in alpine regions. These trends were clearly illustrated by Beale *et al.* (1941), who classified all the plants which had been examined into tropical, sub-tropical and temperate (including alpine) species.

We have similarly classified the eastern Australian species (Table 11) on the basis of the distributions set out in Table 1 and apart from the very low proportion of pelargonidin and the higher proportion of delphinidin already discussed the effect of climate on the occurrence of the anthocyanidin types is clearly in accordance with the earlier findings (Figure 4).

TABLE 11.
Variation of Anthocyanidin Type with Climate.

	Tropical (43 spp.). %	Sub-tropical (42 spp.). %	Temperate (135 spp.). %
Pelargonidin	7	2.5	0.8
Cyanidin	48	48	35
Delphinidin	43	50	65

Notes.

"Tropical" includes the New Guinea species, the tropical Queensland species and the species which range from tropical to sub-tropical.

"Temperate" includes mainly the species which range from sub-tropical to temperate together with the species restricted to the range of latitude 33°–36° S, and some truly temperate species.

The Western Australian species and species with a very wide distribution are not included. The cultivated Australian species are included.

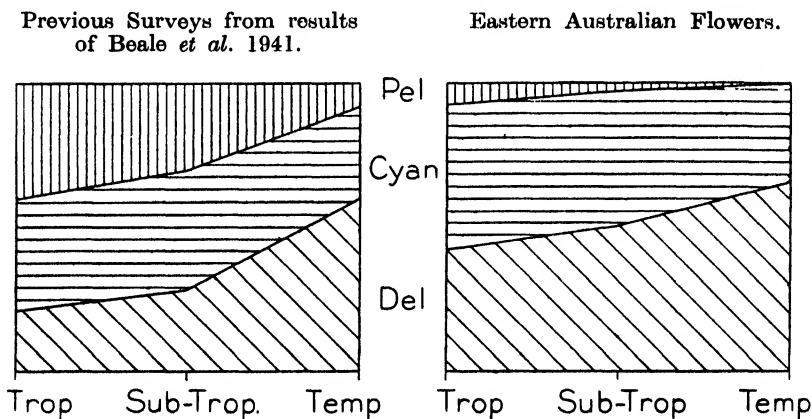


Fig. 4.—Variation of Anthocyanidin Type with Climate.

It should be noted that the plants that we have classified as temperate occur on the sub-tropical side of the temperate zone and include no alpine flora, so the sharp increase in delphinidin in truly temperate species observed by Beale *et al.* is not questioned.

Beale *et al.* found that tropical flowers were redder than flowers of other climates and pointed out that the effect of climate on the distribution of anthocyanidin types is biological rather than chemical. That is, the difference in anthocyanidin distribution is simply the result of different colour ratios in the flowers of different climates. Red pigmentations have a higher biological value than blue in the tropics and sub-tropics but in temperate and alpine climates the value of red apparently decreases and (or) the value of blue increases. There will be several factors controlling the colour ratio in any particular area, the most immediate factor undoubtedly being the colour response of insects and birds.

(Cf. Lawrence and Price, 1940.) It seems likely that the high value of red pigmentations in the tropics is due to the favourable contrast with the pervading green background.

DISTRIBUTION OF ANTHOCYANINS IN FRUITS.

In Table 12 are shown the distributions of anthocyanidins in the fruits of 56 Australian species, of which 85% were wild and, for comparison, the combined results of previous surveys (from the data of Lawrence *et al.*, 1939, and Beale *et al.*, 1941).

TABLE 12.
Distribution of Anthocyanidins in Fruits.

	Australian Species.		Previous Surveys.	
	Number.	%	Number.	%
Pelargonidin	2	3.5	9	16
Peonidin	2	3.5	2	3.5
Peonidin + cyanidin	2	3.5	—	—
Cyanidin	26	46	29	53
Malvidin	11	20	8	15
Methylated delphinidin	2	3.5	—	—
Petunidin	—	—	1	2
Delphinidin	11	20	6	11
Total	56		55	
Pelargonidin Type	2	3.5	9	16
Cyanidin Type	30	54	31	56
Delphinidin Type	24	43	15	27
Degree of Methylation :				
Cyanidin	4/30	13	2/31	6.5
Delphinidin	13/24	54	9/15	60

It will be seen that, as in the case of the flowers, in the Australian species there is a much lower proportion of pelargonidin and a higher proportion of delphinidin type compared with the results of previous surveys. In this case it does not appear justifiable to consider reasons for the difference in view of the small numbers and the fact that the two sets of figures cover, for the most part, different groups of families.

The distribution of anthocyanidins in fruits appears to depend on climate in the same way as in flowers. Thus eight anthocyanidins of delphinidin type were found in 13 species classed as temperate, while only three were found in 21 tropical species. Also, the two pelargonidin-containing fruits were both tropical species.

In eight cases we have examined both the flowers and fruits of a species and in each case the same anthocyanidin was found in both, though in some cases the glycoside types were different.

NITROGENOUS AND ABNORMAL ANTHOCYANINS.

Most of the species listed in Table 1 as containing nitrogenous anthocyanins have already been recorded in previous surveys. The only new species recorded are *Mesembryanthemum aequilaterale* and *Atriplex cinerea*. Nitrogenous anthocyanins have previously been found in other species of both of these genera

(Lawrence *et al.*, 1939). Two other species, *Veronica Derwentia* (252)* and *Solanum aviculare* (250) were found to contain unstable pigments which may have been nitrogenous. It is noteworthy that these belong to orders placed close together in Hutchinson's classification but far removed from the orders known to contain nitrogenous pigments.

No definite indications were found of the occurrence of non-nitrogenous abnormal anthocyanins. In a number of cases indefinite tests were found to fit into a single pattern and were undoubtedly due to interference by other substances in the plant extract. (See note 12 to Table 1.)

MIXTURES OF ANTHOCYANIDINS.

Mixtures of anthocyanidins due to incomplete methylation have already been discussed. In addition to these, thirteen species (included in Table 1) were found to contain mixtures of anthocyanidins of different type in comparable proportions. The classes of mixtures found were as follows:

Cyanidin + pelargonidin	1
Cyanidin + malvidin	6
Cyanidin + delphinidin	5
Cyanidin + a nitrogenous anthocyanin	1

We would not feel justified in drawing any conclusions concerning biosynthesis of anthocyanins from these data. However, the occurrence of a small amount of cyanidin (which may have arisen from a leuco-anthocyanin) with the nitrogenous anthocyanin of *Mesembryanthemum æquilaterale* (55) is interesting and appears to be the first instance recorded of such a mixture.

SUMMARY.

Following on previous surveys by English workers of the occurrence of anthocyanin pigments in flowers a survey has been made of anthocyanins in the flowers of some 300 native Australian species together with a smaller number of fruits.

The results differ from those of the previous surveys in the distribution of the three anthocyanidin types (pelargonidin, cyanidin and delphinidin), the frequency of methylation of these anthocyanidins and the distribution of glycoside types. These differences are tentatively ascribed to the presence of mutant forms in the cultivated plants examined in the previous surveys. Mutation, together with artificial selection, apparently has the effect of increasing the occurrence of pelargonidin and cyanidin at the expense of delphinidin and also the occurrence of diglycosides at the expense of monoglycosides. The same factors may also increase the frequency of methylation.

The variation in the distribution of the anthocyanidin types with climate and also the correlations between anthocyanin and flower colour found in the earlier work are substantiated. The extent of blueing of flower colour appears to depend on the number of hydroxyl groups in the anthocyanin molecule.

Variation of the anthocyanin pigment of a species with locality is limited and is almost entirely restricted to variation in the type of glycoside and the degree of methylation.

ACKNOWLEDGEMENTS.

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* Hutchinson's number for the family is given to facilitate reference to Table 1.

indebted particularly to Mr. O. D. Evans and to the staff of the National Herbarium, Sydney. We wish to thank also the Directors of the Botanic Gardens of Sydney, Melbourne and Brisbane for provision of most of the cultivated species.

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THE ESSENTIAL OIL OF A PHYSIOLOGICAL FORM OF
BORONIA LEDIFOLIA (GAY).

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The botany of *Boronia ledifolia* (Gay), a small, erect Rutaceous shrub with bronze green leaves and deep pink flowers, is described in Benthams "Flora Australiensis", Vol. 1, page 314. Varieties are also described, e.g. *triphylla* and *rosmarinifolia*.

Boronia ledifolia (Gay) is widely distributed, extending from Port Jackson, N.S.W., to central Queensland. The Queensland plant is mostly var. *rosmarinifolia*.

During a visit to Grafton, N.S.W., in September, 1941, Mr. J. Pocock of The Punchbowl directed our attention to a strongly scented *Boronia*, from which he had distilled some oil. A cursory examination of the leaves and terminal branchlets of this attractive shrub confirmed Mr. Pocock's observations. The overpowering aroma, resembling the constituents of oil of Rue, differentiated this *Boronia*, which superficially resembled *B. ledifolia* (Gay) from any similar *Boronias* previously examined by us.

We have since examined the foliage of *Boronia ledifolia* (Gay), *B. ledifolia* var. *triphylla* and *B. ledifolia* var. *rosmarinifolia*, but their lower contents of oils of dissimilar composition readily differentiated the *Boronia* at The Punchbowl, via Grafton, N.S.W.

No doubt morphological differences will subsequently be noted, but pending further botanical investigation we prefer to call this *Boronia B. ledifolia* variety "A", particularly in view of the reports received from our botanical colleagues, Mr. C. T. White, F.L.S., Government Botanist, Brisbane, Q., and Mr. R. H. Anderson, Chief Botanist and Curator, Botanic Gardens, Sydney.

Both botanists expressed the opinion that our specimens were *Boronia ledifolia* (Gay), but Mr. White added this note, viz. :

"Your plant in some ways is intermediate between *B. ledifolia* and the variety *rosmarinifolia*. *Boronia ledifolia*, like *B. pinnata*, is one of those species of which there are a great many forms which may be treated as species, though some run into one another, and the group is a particularly difficult one."

Through the courtesy of Mr. J. Pocock, who provided not only the original specimen of oil but also several consignments of leaves and terminal branchlets, we were enabled to investigate the chemical nature of the essential oil. The whole of the material received at intervals during the past seven years was collected from the one locality near Grafton, N.S.W., where it occurs somewhat sparsely. Efforts to obtain larger quantities of foliage in order to determine the minor constituents of the oil were frustrated by bush fires.

THE ESSENTIAL OILS.

The essential oils obtained from the various consignments enumerated in the accompanying table were of a very pale lemon tint, and possessed the characteristic odour of the principal constituents, methyl n. heptyl ketone and methyl n. nonyl ketone. These two substances constitute about 75% of the oil, the unidentified substances being most probably α -pinene, sesquiterpenes and the methyl ester of anthranilic acid.

The essential oils obtained from *Boronia ledifolia* (Gay) and *B. ledifolia* var. *triphylla* differ markedly both in yield of oil and in chemical composition, from the essential oil derived from the physiological form collected at The Punchbowl near Grafton, N.S.W.

Although these samples were too small for a detailed chemical examination (they measured 8 mls.), preliminary tests confirmed the presence of terpenes and sesquiterpenes and the absence of the characteristic constituents of *B. ledifolia* (Gay) var. "A".

EXPERIMENTAL.

The 160.5 lb. weight of leaves and terminal branchlets yielded on distillation with steam, crude oils, which on examination gave the chemical and physical characters shown in accompanying table. Similar constants have been included for oils obtained from *B. ledifolia* (Gay) and *B. ledifolia* var. *triphylla* for comparative purposes.

All distillates were subjected to repeated fractional distillation, usually at 10 m.m., but only one is recorded, viz. 1/9/1947. The crude oil was distilled through a 60 cm. Vigreux column with a Weir reflux head at total reflux, with intermittent take-off.

Fraction.	b.p.	Pressure.	Bath. Temp.	Vol. ml.	d_{15}^{15}	α_D^{20}	n_D^{20}
1	178°	770 mm.	278°	6.5	0.8476	+10.72°	1.4436
2	185°		283°	8.0	0.8420	+6.4°	1.4365
3	189-190°		290°	6.0	0.8364	+3.0°	1.4290
4	79°	10 mm.	196°	14.0	0.8299	+0.25°	1.4228
5	88°		244°	8.0	0.8299	± 0	1.4230
6	104°		272°	15.0	0.8367	± 0	1.4311
Residue					0.9050	± 0	1.4730

DETERMINATION OF THE KETONES.

A carbonyl estimation on the crude oil showed the presence of about 72-75%, calculated as methyl n.-nonyl ketone.

Identification of Methyl n.-heptyl ketone.

Fraction 4 (1 ml.) on treatment with semicarbazide hydrochloride reagent gave a white crystalline precipitate in good yield. On recrystallisation from boiling aqueous alcohol, flat, rhomboidal monoclinic crystals were obtained melting at 119-120° C.

TABLE 1.
Boronia ledifolia (Gay) Variety "A".

Date.	Locality.	Weight of Leaves.	Yield of Oil.	d_{15}^{15}	α_D^{20}	n_D^{20}	Ester No. 1½ Hours Hot Sap.	Solubility in 70% Alcohol W.W.	Remarks.
17/ 9/1941	The Punchbowl, near Grafton, N.S.W.	Sample of oil.		0.836	-0.03°	1.4289	23.5	Vol. 1.0	Oil distilled and submitted by Mr. J. Pocock.
26/11/1941	" "	40 lb.	0.12%	0.8354	-1.54°	1.4266		1.0	Distilled by Mr. J. Pocock. Yield considered low through dry conditions and plant past flowering.
11/11/1942	" "	18 lb.	0.46%	0.852	-0.75°	1.4341		1.0	Plants in full flower and very good condition.
2/ 8/1946	" "	23 lb.	0.19%	0.8511	Inactive	1.4375		1.0	
1/ 9/1947	" "	79½ lb.	0.23%	0.8448	-2.88°	1.4364		1.0	
<i>Boronia ledifolia</i> var. <i>triphylla</i> .									
13/ 8/1947	National Park, near Sydney.	29 lb.	0.06%	0.9080	-22.3°	1.4850		<i>Insol.</i> 10 vols. 80% alcohol, W.W.	Collected by S. Smith-White. Fresh leaves and terminal branchlets. Plants profusely flowering.
<i>Boronia ledifolia</i> (Gay).									
16/ 1/1948	Cowan, N.S.W.	29 lb.	0.06%	0.9130	-27.2°	1.4819		<i>Insol.</i> 10 vols. 80% alcohol, W.W.	Whole plants collected by S. Smith-White and H. H. G. McKern.

Found: C, 59.84; H, 10.6; N, 20.93. Calculated for $C_{13}H_{21}ON_3$: C, 60.24; H, 10.62; N, 21.09.

On treatment of 1 ml. with 2:4 dinitro-phenylhydrazine reagent, yellow flakes were obtained in good yield, which on recrystallisation from aqueous alcohol melted at 57–58°.

Found: C, 55.32; H, 6.82; N, 17.27. Calculated for $C_{15}H_{23}O_4N_4$: C, 55.86; H, 6.75; N, 17.39.

These results, together with the physical constants, show the ketone to be identical with methyl n.-heptyl ketone.

Identification of Methyl n.-nonyl ketone.

Fraction 6 (1 ml.) on treatment with semicarbazide hydrochloride reagent gave a good yield of crystalline semicarbazone, of melting point 122–123°. A mixed melting point determination with an authentic sample semicarbazone of methyl n.-nonyl ketone gave the same result.

Found: C, 63.09; H, 11.12; N, 18.30. Calculated for $C_{12}H_{25}ON_3$: C, 63.37; H, 11.08; N, 18.47.

The 2:4 dinitro phenylhydrazone was also prepared. On recrystallisation from aqueous alcohol, the crystals melted at 62–63° C. A mixed melting point determination with an authentic sample of the 2:4 dinitro phenylhydrazone of methyl n.-nonyl ketone showed no change of melting point.

UNIDENTIFIED CONSTITUENTS.

Owing to the limited quantity of oil available, it was not practicable to isolate the minor constituents. Redistillation of fraction 1 gave 2 mls. of oil (b.p. 146–162, $d_{15}^{15} 0.8525$, $\alpha_D^{20} +16^\circ$, $n_D^{20} 1.4521$) which probably contained α -pinene. The presence of sesquiterpene was indicated by the formation of a purple colour by the action of bromine vapour on solution of the residual fraction in glacial acetic acid. The residual fraction exhibited strong fluorescence under ultra-violet light, and possessed the characteristic odour of methyl anthranilate. Efforts to isolate the ester were not successful.

ACKNOWLEDGEMENTS.

Our thanks are due to Mr. J. Pocock, of The Punchbowl, N.S.W., for bringing this Boronia and its essential oil under our notice, and for supplying leaves and terminal branchlets for subsequent investigation.

We are also indebted to Miss J. Fields, of the Organic Chemistry Department of the University of Sydney, for the micro-combustion results, and to our assistants, Mr. H. H. G. McKern, A.A.C.I., and particularly Mr. K. G. O'Brien, B.Sc., for much valuable help in completing the investigation.

SPECTROSCOPIC ANALYSIS OF ALLOY STEELS.

By C. JAMES,

The Commonwealth Steel Co., Waratah.

Communicated by S. C. BAKER.

With Plate VII and one text-figure.

Manuscript received, April 23, 1948. Read, June 2, 1948.

Schliebmann (1934) and Emery (1941) have published details of visible spectrum lines employed for qualitative spectroscopic analysis of steels. The spectra of the high alloy steels manufactured by the Commonwealth Steel Co. differ considerably from these and from the charts supplied by Adam Hilger Ltd. with the "Spekker" Steeloscope, which may be described as a spectroscope with two large prisms in tandem having ample resolution for ferrous work in the visible region of the spectrum and robust enough for use on a steel plant.

Approximately 130 alloy steels are manufactured by the Commonwealth Steel Co. and about half of these can be positively identified with the Steeloscope alone; the remainder can be classified into groups. Typical analyses of three main types of steels are given in Table I. The spectroscopic examination is

TABLE I.
Typical Analysis of Main Types of Alloy Steels.

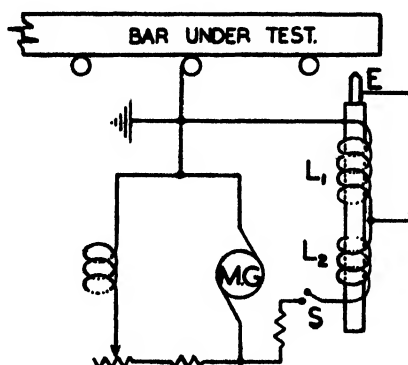
Grade.	C.	Si.	Mn.	P.	S.	Ni.
P10	% 0.9-1.1	% 0.80 max.	% 11.0-13.5	% 0.075	% 0.04	% 3.5-4.5
F2	0.14 max.	0.5-0.8	0.6-0.80	Low	Low	9.50-10.50
B1	0.78-0.84	0.30 max.	0.40 max.	0.020	0.020	0
Grade.	Cr.	Mo.	W.	Va.	Co.	Ti.
P10	% 0	% 0	% 0	% 0	% 0	% 0
F2	17.5-18.5	0	0	0	0	0.5-0.8
B1	4.2-4.7	0	21.0-22.0	1.0-1.5	11.5-12.5	0

mainly a final check against mixed bars before shipment; it is also used for qualitative work such as the identification of a "lost" bar. The success of the Steeloscope depends largely on the skill and experience of the operator but the principles of the identifications can be seen from a study of Table I. Thus only F2 contains titanium; only B1 contains cobalt, etc. Then again only a few steels contain molybdenum and this is usually in conjunction with nickel and

chromium. Further separation is achieved by the quantitative estimations detailed below. On an average day one operator examines about 800 bars for the presence or absence of at least nickel, chromium and molybdenum.

OPERATING TECHNIQUE.

The bars, billets and blooms in sizes varying from $\frac{3}{8}$ in. to 7 in. round or square with average length about 15 feet are brought to the Steeloscope by overhead crane direct from processing and placed on an elevated table. From there each bar is placed in turn on rollers in a channel leading to the arc unit, which is illustrated by the diagram. Essentially the arc unit consists of a pair of vertical solenoids, L_1 and L_2 , having a common iron armature to which a $\frac{3}{8}$ in. Armco iron electrode, E , is attached; this is the live electrode and is negative; it is directly beneath the bar under test. When the magnetically operated push button switch, S , is closed, both solenoids are energized, causing E



Circuit Diagram of Arcing Table.

to contact the bar, thereby short-circuiting L_1 , so that E drops a short distance thus striking the arc. Suitable limit resistances are included to give an arc current of 8 amperes. Power is supplied by a motor-generator set, MG , delivering 240 volts D.C. Thus the operator merely presses S to strike the arc, and handling is very rapid.

SPECTRUM LINES EMPLOYED.

Most of the work is done in the 4708A to 4719A section of the spectrum because this enables the determination of the main elements without moving the eyepiece of the Steeloscope; the lines used are listed in Table II and are shown in the Plate. When present molybdenum is always estimated with the "confirmative" line 5533A because of the closeness of Mo 4717.9 and Cr 4718.5. Nickel is frequently difficult and the presence of scale and oil on the bar make it desirable to check the estimation with the Ni 5081 "confirmative" pair.

TABLE II.
Spectrum Lines Employed.

4708-4719A Lines.	Confirmative Lines.	Other Elements.
Cr 4708.04 and 4718.45 Mo 4717.92 Mn 4709.7 Ni 4714.42	Mo 5533.0 Ni 5080.5 and 5081.1 ----	Co 4867.9 Ti 4533 Va 4408.52 W 5514

Vanadium, tungsten, titanium and cobalt are checked individually with the lines headed "Other elements" in Table II; they are marked in the Plate.

Carbon steels present difficulties when the alloy constituents do not vary and the carbon does. In such cases the carbon can be estimated by the colour and form of the sparks thrown from a small high-speed grinding wheel pressed against the bar.

The silicon lines used by Schliebmann do not appear with the concentrations and set-up employed here; unfortunately, too, silicon throws a spark from the grinder that is indistinguishable from that of low concentration tungsten. Thus silicon is the only important element that cannot be estimated with the Steeloscope.

QUANTITATIVE ESTIMATIONS.

Chemical checks have shown that an experienced operator can make certain quantitative estimations with a fair degree of certainty using the Steeloscope on the works.

The minimum concentrations of the alloy constituents necessary for positive identification are listed in Table III. Thus if, for example, a bar contained 0.5% tungsten, the Steeloscope operator would not see the tungsten line and would record tungsten as absent. Cobalt is not included in this table because low concentrations have not been encountered.

TABLE III.
Minimum Concentration for Identification.

	%		%
Cr	0.05	Ti	0.15
Mn	0.10	Va	0.15
Mo	0.06	W	1.0
Ni	0.3		

Manganese.

The majority of steels contain 0.3% to 0.8% manganese, and by estimating the intensity of Mn 4709.7 it is easy to distinguish 0.3%, 0.5% and 0.8%. A few steels contain up to 12% and these are readily recognized.

Chromium.

The majority of steels contain 0.4% to 1.2% chromium; only Cr 4718.5 appears when there is less than 0.5%, but when the chromium content exceeds 0.5% the Cr 4708.0 line appears and its intensity enables the separation of 0.8% from 1.2%. Other steels contain 14% to 25% chromium and still using Cr 4718.5 one can say whether the concentration is nearer to 14% or to 25%.

Molybdenum.

Only a few steels contain molybdenum, and in these it is quite easy to distinguish 0.1%, 0.2% and 0.3% using Mo 5533.

Nickel.

In nickel steels containing 3% nickel all three of the lines in Table I may look much brighter than in another type of steel containing 8% nickel; but within a given grade 0.3%, 1.5% and 3.0% can be separated using any of the lines in Table II, but the 5081 Ni pair is preferred. When 20% nickel is present the Ni pair are about the same intensity as neighbouring iron lines; over 20%

they are much stronger and under 20% much weaker than the iron lines. Usually, too, high nickel content is associated with high chromium content and *vice versa*, so that a nickel estimation can often be checked by estimating the chromium.

ACKNOWLEDGEMENTS.

I wish to thank the Management of the Commonwealth Steel Co. for permission to publish this paper and the Physics School of the Newcastle Technical College for the use of their Hilger "Wavelength" spectrometer in the selection of the spectrum lines employed and the preparation of the Plate.

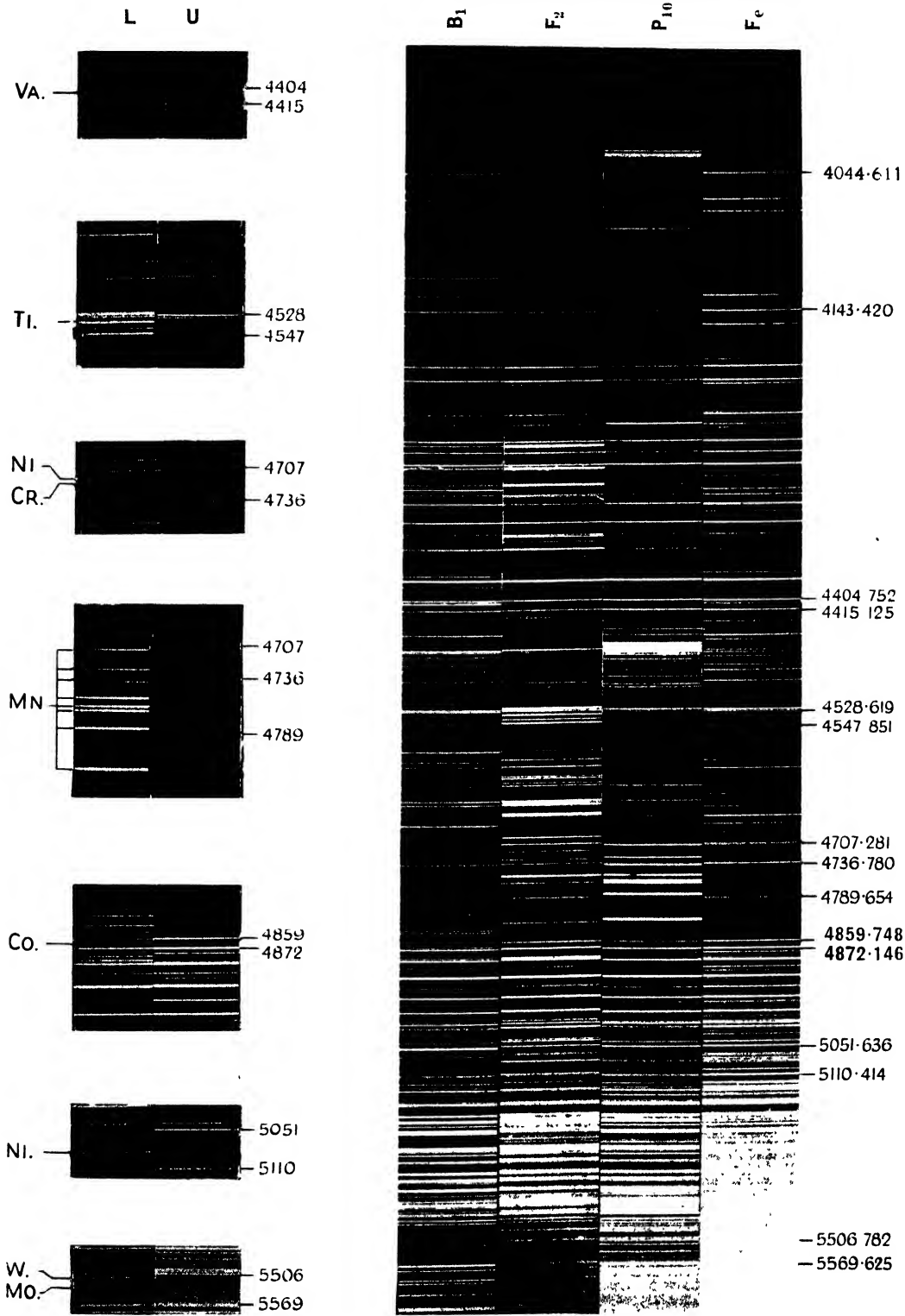
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EXPLANATION OF PLATE.

The visible spectra of the three alloy steels of Table I are shown, together with a spectrum of Armco iron, to serve as a wavelength scale.

Sectional enlargements of the analytical spectrum lines, together with the corresponding sections of the iron spectrum, enable the selection of the analytical lines in the spectra of the three steels selected.



NITROGEN IN OIL SHALE AND SHALE OIL.

I. THE NITROGEN COMPOUNDS PRESENT IN KEROGEN.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., M.Inst.Pet.

Manuscript received, April 29, 1948. Read, June 2, 1948.

Although oil shale deposits have been exploited for about a century, little is known about the constitution of the organic portion or kerogen of the shales, and even less appears to be known about the origin or nature of the nitrogenous constituents of the kerogen.

TABLE 1.
Ultimate Analyses of Kerogens.
(Re-calculated to Ash-free Basis.)

Shale.	Australian.				American.				Scottish. Typical.	Estonian.
	Maran- garoo Rich.	Joadja Creek.	Glen Davis.	Newnes.	Ken- tucky.	Colo- rado.	Utah.	Nevada.		
% C.	84.20	80.6	85.1	81.9	79.0	79.3	80.5	82.3	80.02	77.2
% H.	11.83	12.9	10.6	10.2	8.3	10.5	9.8	8.2	7.65	9.2
% N.	0.81	0.3	1.3	0.8	2.2	2.6	2.7	1.7	2.30	0.4
% S.	1.02	0.3	0.5	0.7	2.3	1.2	1.5	4.3	0.61	2.0
% O.	2.54	5.9	2.5	6.4	8.2	6.4	5.5	3.5	9.42	11.2
Reference	1	2	3	4	4	4	4	4	5	6

The nitrogen content of kerogen varies with and in each deposit and ranges from about one-fifth of one per cent. to nearly three per cent. of the kerogen by weight (Table 1). When the origin and properties of kerogen are discussed the nitrogen-containing materials present are usually overlooked. However, this should not be so, as quite small amounts of nitrogen can be associated intrinsically with quite large amounts of material. For example, a nitrogen content of three per cent. is equivalent to the presence of nearly twenty per cent. of protein matter (see Table 2).

TABLE 2.

Source of Nitrogen.	Nitrogen Content.	Amount Equivalent to 1% of N.
Chlorophyll a	7.1%	14.0%
Chlorine e (a degradation product of chlorophyll)	9.4%	10.5%
Protein	16.0%	6.25%

Before we can advance very far in the elucidation of the nature of the nitrogen compounds present in kerogen it is essential that we first review the evidence on the origin and nature of the kerogen itself. The original suggestion of Professor David (7) that the torbanites of New South Wales are of algal origin is now generally accepted. Twenhofel (8) and Dulhunty (9) have suggested that periodic growth of algæ built up layers of organic débris in lakes. After burial this was changed to torbanite by polymerization of the algal substance and the pressure of the overlying sediments. The modern counterparts of such lakes exist in the south-west of Western Australia and in the Coorong district of Victoria in Australia, and in Lake Bal in Siberia.

At this stage it is of interest to note that highly organized plants contain much less nitrogen than the more lowly organized plants. Thus bacteria contain up to 13%, algæ 3.2 to 4.8%, and typical swamp plants about 1.6% nitrogen (10).

Not all oil shales, however, are of algal origin; for example, the shale from Orepuki, New Zealand, "consists mainly of what would appear to be completely macerated plant débris" (11), while the kerogen of Tasmanian oil shale is predominantly a spore material (12). In discussing the origin of petroleum, Wilcox (13) explains the origin of oil shales as buried lake muds in which high molecular weight organic material remains to form some part of the final product of the squeezing and hardening process, during which petroleum may have been expressed. This American viewpoint is of interest owing to the enormous oil shale reserves of the United States of America, most of which are, however, of low grade.

Carlson (14) conceived the structure of the kerogen of the American shales he examined as that of a long chain fatty acid combined with an inorganic base.

Cane (1), working on the torbanites of New South Wales, has extended and combined the theories of Dulhunty and Carlson by suggesting that "kerogen has been formed from fatty acids produced from algal detritus by the removal of carbohydrates and protein matter by bacterial decomposition. The remaining fats are presumed to have been extensively hydrolysed to the free acid." This, however, need not mean that kerogen consists entirely of polymerized fatty acids, or that it is free from carbohydrates and proteins. However, the Carlson-Cane theory of the nature of the kerogen does not account for the presence of nitrogen in the shale except as incidental matter.

From a microscopic examination of the New South Wales torbanites, Dulhunty (15) has described five distinct organic constituents, of which gelosite and retinosite usually occur as minute rounded globules resembling organic cells packed together. The difference between these two constituents appears to be biological rather than environmental (16) and they would presumably be the Carlson-Cane polymerized fatty acid material.

The torbanites of New South Wales are frequently associated with cannel coal, one often changing into the other in the deposit, although the constitution of the two materials is quite distinct (16), the organic constituents of the cannel coal being of vascular plant origin and include spore material, pollen and resin. When cannel coal is closely associated with the torbanite the two are usually mined and retorted together for the production of oil.

Conacher (17) remarks that the nitrogen in the kerogen appears to originate wholly or mainly from the vegetable débris from which the kerogen was formed. The vegetable nature of the nitrogenous constituents of kerogen is supported by the work of Steuart (18), who distilled an artificial shale oil from a mixture of lycopodium dust and Fuller's earth. The oil contained nitrogen compounds and was similar to Scottish shale oil.

The nitrogen compounds present in the vegetable débris, which was the pregenitor of the kerogen, could be of alkaloidal, porphyrinic (chlorophyll) and protein origin.

ALKALOIDAL NITROGEN.

Since oil shale is considered to be formed principally as lake muds, etc., the alkaloidal origin of at least the major portion of the nitrogen is immediately precluded as "alkaloids are found almost exclusively in the seed bearing plants" (19). No further consideration is therefore given to this possible, but improbable source, although, since they are more resistant to decay, any alkaloids which may be present would tend to accumulate in the kerogen.

PORPHYRINIC NITROGEN.

Treibs (20, 21, 22, 23) identified porphyrins in a wide range of organic minerals including oil shales, oil slates, cannel and other coals, crude oils, etc.

The porphyrinic material was extracted from the extremely finely divided shale with chloroform, benzene or glacial acetic acid. The extracted material was fractionated by extraction with hydrochloric acid and purified by crystallization or chromatographic adsorption. The porphyrin complexes identified

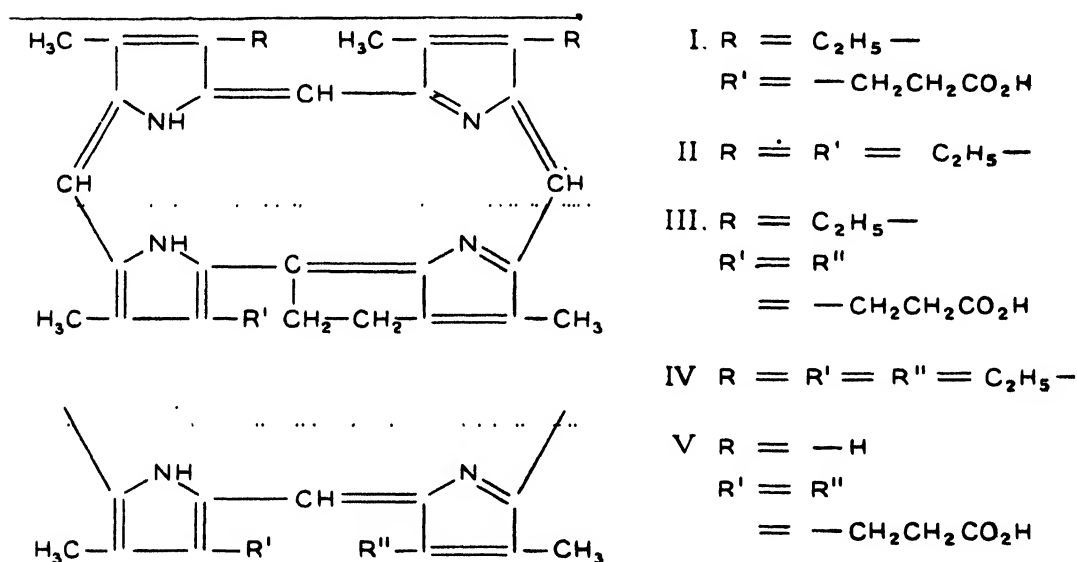


Fig. 1.—Porphyrins Detected in Shales by Treibs (19, 20, 21, 22).

by their absorption spectra were desoxo-phyllerythrin (I), desoxophyllerythro-ætioporphyrin (II), mesoporphyrin (III), meso-ætioporphyrin (IV) and deuterio-ætioporphyrin (V). The greatest amount of porphyrin complexes was found in an oil slate from Switzerland which contained 0.34–0.40%. The main complex present in this slate was found to be in the form of a vanadyl complex. Ferric complexes of the porphyrins were found in some Bavarian shales.

Treibs suggested a mechanism for the formation of these porphyrins from chlorophyll and demonstrated its practicability. By slowly heating pheophytin in petroleum to 250°–320° C. phylloerythrin was obtained, and further heating to 360° C. gave desoxophyllerythro-ætioporphyrin (22), which was the main constituent of the porphyrins isolated from the shales. Although this method employed a relatively high temperature, it is probable that, in the formation of the shales, etc., the reaction was biochemical rather than thermal as the occurrence of the acid porphyrins excludes temperatures of formation greater than 200° C.

Treibs (23) also observed the presence of green pigments associated with the porphyrin complexes and he found that they were present in sapropels, although the porphyrins were absent. It would appear that these pigments consist of chlorophyll and/or its initial degradation products. This suggestion is supported by the observation of Wells and Erickson (24), who reported the presence of chlorophyll in a lake bottom mud.

Pestovskii, Bednyagina and Mikhailova (25) observed that the precursors of thiophenes which appeared on the distillation of some Ural crude oils appeared to have been derived from porphyrins in the crude oil by the conversion of the pyrrole rings into thiophene rings. The mechanism of the change was envisaged to have been due to the presence of hydrogen sulphide from the fermentation of the original organic deposit, and the catalytic influences of the rocks, etc. It is quite feasible that some of the porphyrinic constituents of the kerogen may have been similarly modified to give complex nitrogen- and sulphur-containing materials of the same general structure.

Despite the proven presence of porphyrinic nitrogen compounds in many oil shales, the amounts found to be present have been far from sufficient to account for the high nitrogen content of the kerogens.

PROTEIN NITROGEN.

There is apparently no record in the literature of protein matter or its degradation products having been detected in shale, although the nature of the precursors of the kerogen indicated that proteins were most certainly present in the original deposits. Also it is doubtful whether they were more than partially removed or transformed by the biological processes involved in converting the original algal, spore or other plant material into kerogen.

In general, it appears that the kerogen of shales has probably undergone less biochemical decomposition than the organic constituent of coal. It is therefore of interest to note that a school lead by Terres (26) regards the protein matter of dead microorganisms as an important source material of coal, thus accounting for the relatively constant and high percentage of nitrogen found in coal.

Waksmann (27) has shown that lignin tends to form complexes with proteins. These complexes are highly resistant to plant decay and might well influence the retention of nitrogen compounds in the shale on maturing.

Also, Maillard (28) has found that humus-like compounds were readily obtained by the condensation of sugars with amino acids, a reaction which has been observed to take place at temperatures as low as 37° C. ; and these products readily yielded cyclic nitrogen compounds on heating.

Jodidi (29) found amides and mono and diamino acids in peat. Shacklock and Drakeley (30) applied Jodidi's technique to coal with the same results, and found that the amount of nitrogen extractable with boiling dilute acid decreased with increasing rank of the coal.

A long series of nitrogenous compounds including proteins, amino acids, amides, amines, purines, pyrimidines, pyridine derivatives, chitin and nucleic acids has been isolated from soil humus, humic acid preparations and peat and is quoted as proof of the protein nature of the younger fossil fuels (10).

A very small amount of the nitrogen in coal has been shown to be directly attached to a benzene ring by the isolation of 2.4.6 tribrom aniline from the products of the alkaline hypobromite oxidation of coal (31). This could be explained by the oxidative bromination (via anthranilic acid) of tryptophane residues from the protein in the material from which the coal was formed.

Indirect, but also rather inconclusive evidence for the presence of protein in kerogen is that ammonia, which is almost invariably present among the

pyrolytic decomposition products of protein (32), is also produced during the entire course of the pyrolysis of kerogen (33), though mainly at the higher temperature (34).

The presence of pyridine derivatives in coal (35, 36) as well as in humus and peat (10) could be explained by the condensation of proteins and amino acids with aldehydes and ketones during the degradation of the original organic material.

The material obtained by ether extraction of Glen Davis torbanite which had been dehydrogenated with sulphur at 150°–155° C. until there was no further evolution of hydrogen sulphide, was a light brown, low viscosity oil with a strong pyridinic odour (37). From the low temperature employed this can probably be taken as evidence of the presence of some pyridine ring systems in this kerogen.

The available evidence concerning the presence of protein material in kerogen is far from conclusive, though it appears that, in the absence of any other likely and abundant source material the bulk of the nitrogen in the kerogen has had its origin as such. The original proteins have probably been extensively modified during the biochemical conversion of the deposits into oil shale by deamination and decarboxylation, and by condensation with aldehydes and ketones, etc., produced during the process. Such modified proteins would be quite insoluble in various solvents, and this is in keeping with the properties of kerogen.

It is obvious that, if any light is to be shed on this problem of the nitrogenous constituents of kerogen, much more work on the subject is necessary. Consideration of the pyrolytic decomposition products of proteins and porphyrins can be expected to give some further but indirect evidence of the nature of the nitrogenous constituents of the kerogen, and will be discussed in a later paper.

SUMMARY.

The nitrogen content of shale kerogens is far from insignificant and appears to be of porphyrinic (chlorophyll) and protein origin. Treibs has identified small amounts of several porphyrins in oil shales but in quantities too small to account for more than a fraction of the total nitrogen present. It is suggested that the bulk of the nitrogen of the shale kerogen is of protein origin and has been extensively modified during the kerogen formation.

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NITROGEN IN OIL SHALE AND SHALE OIL.

II. ORGANIC NITROGEN COMPOUNDS IN SHALE OIL.

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Despite the fact that many workers have examined the organic nitrogen compounds from shale oil, relatively few of the bases have been isolated and positively identified. This has been due mainly to the complex and unstable nature of the materials being handled, and to the fact that ammonia has been the only commercial nitrogenous product obtained from shale.

Primary, secondary and tertiary bases have been detected as classes, while quaternary bases have been suspected but not proved (1). An extensive survey of the literature has failed to reveal the isolation or identification of any primary or secondary amine from shale oil. Of the tertiary amines only pyridine bases have been isolated, though isoquinoline and quinoline homologues have been claimed.

The different classes of bases will be discussed in turn.

PRIMARY AMINES.

Horne, Finley and Hopkins (1) detected only traces of primary amines in the bases from the gasoline fraction of a shale oil by Hoffman's carbylamine reaction.

McKee (2) found only traces of primary amines when investigating the reaction of the bases from De Beque (Colorado) shale oil with nitrous acid.

SECONDARY AMINES.

Almost every investigator who has examined the tar bases from shale oil has obtained positive evidence for the presence of pyrroles as a group.

They are generally detected by means of the pine shaving test, though all general reactions of the pyrroles have been obtained (1, 3, 4). Despite the fact that Williams in 1854 (5, 6) was the first to detect them, the only attempt that appears to have been made to give any more than a cursory examination of this class of bases (1) failed, owing to the crude bases (boiling range 195°–250° C.) decomposing on vacuum distillation to give ammonia, free carbon and tertiary amines.

McKee (3) considered it probable that the higher boiling secondary amines were hydrogenated pyridines, though no evidence was presented to support this view.

In order to test for the presence of hydrogenated quinolines in Tasmanian shale oil, Cane (4) checked the refractive index before and after dehydrogenation of the purified bases with selenium. From his results he deduced that there were no hydrogenated quinolines present. Cane suspected the presence of a piperidine nucleus in the secondary bases, but the dehydrogenation of any

piperidines present would have had the same effect in increasing the refractive index as the hydrogenated quinolines so these too must have been absent.

Apparently no dialkyl, alkaryl or diarylamines have been detected in shale oil, so it appears that most, if not all, of the secondary amines present are pyrrole derivatives.

TERTIARY AMINES.

Reference to the occurrence of tertiary bases in shale oil are numerous, but relatively few investigators have succeeded in isolating any of the pure bases.

Different workers have claimed to have identified bases of the pyridine, quinoline and isoquinoline series. The available evidence in each of these classes will be examined in turn.

Because of the very much greater chemical and thermal stability and basic characteristics of these compounds, as compared with the secondary amines present in shale oil, they have been easier to separate from the oil and examine. This explains why the bulk of the work done has been on these compounds.

PYRIDINES.

Williams, in 1854 (5, 6), was the first investigator to isolate and identify pyridine bases in shale oil. From the ultimate analyses of the platinichlorides of the fractionated bases he detected picoline, lutidine, collidine and parvoline. By fractional crystallization of the platinichloride of that portion of the bases boiling below 210° F. he obtained fractions whose platinum content corresponded with the platinichlorides of lutidine, picoline and pyridine. Since this work was carried out well before there was knowledge of the isomeric forms of the higher bases, we can say that the only pure base Williams detected was pyridine.

Garrett and Smythe (7, 8) isolated and examined the bases from the lower boiling fractions of Scottish shale oil and identified pyridine, α picoline, four lutidines and γ collidine. They were unable to identify any of the components of the higher cuts as they could not obtain crystalline derivatives.

Discussing Scottish shale oil, Smith and Peutherer (9) state that "nitrogen present in the shale oil . . . exists mainly as basic compounds such as pyridine and its derivatives."

Horne, Finley and Hopkins (1), working on the oil from an American shale, were unable to isolate pure pyridine by fractional distillation of their basic oil, but they isolated and identified α picoline. Another fraction proved to be β and/or γ picoline, but the identification was not carried further. Lutidine, collidine and parvoline fractions were also obtained and analysed but they did not isolate or identify any pure member of this series.

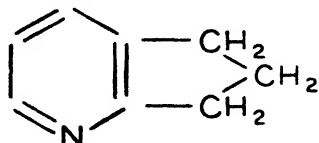
McKee (2) examined the bases from De Beque, Colorado, shale oil and concluded that the bases boiling up to 390° C. were "mostly methylated pyridines and closely related compounds" and not quinolines. The only individual base that he identified was 2.4.6. trimethyl pyridine.

Kogerman (10) examined the bases from Estonian shale oil and, although he classified them as belonging to the pyridine and quinoline series, he did not prove his classification.

Cane (4) isolated and identified 2.4.6. trimethyl pyridine in the bases from a specially prepared crude oil from Tasmanian spore shale.

In a thorough examination of the bases present in Fushun shale oil Eguchi (11, 12, 13) isolated and identified eighteen pyridine homologues though he did not detect pyridine itself. He also isolated a 2.3.6 dimethyl ethyl pyridine but did not establish its full configuration.

Eguchi (13) also isolated a 2,3 disubstituted pyridine with the formula C_8H_8N which he called "pyrindane". In order to account for its properties he tentatively assigned it the structure



Thompson and Bailey (14) confirmed the structure of this base by synthesis and called it 5.6 dihydro pyrindene.

	Thompson's 5.6 Dihydro- pyrindene.	Eguchi's Pyrindane.
Boiling point	199° C. at 750 mm.	199·8° C. at 761 mm.
Melting point of picrate ..	187° C.	181° C.
Refractive index	1·5407	1·541

This base belongs to a new class of bicyclic nitrogen compounds and appears to be the first of the class to have been obtained from any source.

Dodonov and Soshestvenoskaia (15) examined the bases from a bituminous shale from the middle Volga region. They isolated and identified with certainty pyridine, two picolines and three lutidines.

From De Beque (Colorado) shale oil Stauffer (16) isolated a series of pyridine bases from C_7 to C_{13} and identified 2.4.6 trimethyl pyridine and 2 methyl 5 ethyl pyridine. The iodine numbers of the fractionated bases indicated the presence of some unsaturated side chains.

In recent work at the Oil Shale Research and Development Laboratories of the U.S. Bureau of Mines (17) on the bases present in shale naphtha the ultra-violet absorption spectra, boiling points and refractive indices indicated the presence of 2 methyl, 2.4 dimethyl and 2.4.6 trimethyl pyridines in different fractions.

Lanin and Pozhil'tsova (18) investigated the bases present in the tar from the carbonization of sapropel of the Karasine lake region of the Luga region, U.S.S.R. Primary and secondary amines were absent, but eleven pyridine homologues were isolated and identified. This work is of interest here as the sapropel may be considered as an oil shale in the process of formation.

The bases isolated from and identified in shale oils are listed in Table 1.

QUINOLINE BASES.

Several investigators have stated that quinoline homologues are present among the bases from shale oil (4, 10, 19, 20).

Gavin (19) loosely describes the bases from shale oil as pyridine and quinoline homologues, but McKee (2) says that "it is highly improbable that quinolines . . . and their hydroderivatives are present in more than very small amounts in (De Beque) shale oil".

Kogermann (10) claimed that bases from Estonian shale oil belong to the pyridine and quinoline series, though he did not confirm this statement.

Cane (4) appears to be the first investigator to have claimed the isolation of a quinoline base from a shale oil. After purification of one fraction of the bases from Tasmanian shale oil the refractive index and specific gravity fell within the range of the trimethyl quinolines; but, however, a close examination of his paper throws very serious doubt on the validity of his claim to have identified the base as a quinoline derivative.

Cossettini (20) reports that pyridine and quinoline bases are manufactured for pharmaceutical use from the oil-bearing shale from the Rescutta mine at Mt. Salvotti. Unfortunately the original paper was not available but from the abstract it seems that it gives merely a general and brief description of the process and products which have not necessarily been specifically characterized.

TABLE 1.
Tar Bases from Shale Oil.
(The numbers refer to the appropriate references.)

Base.	Identified in Shale Oils.	Sapropel Tar.
Pyridine	5, 6, 7, 15	—
2 Methyl pyridine	1, 7, 12, 15, 17	—
3 " "	12, 13, 15	18
4 " "	12, 13	—
3 Ethyl pyridine	—	18
2 Butyl pyridine	—	18
2.3 Dimethyl pyridine	8, 12	—
2.4 " "	7, 12, 15, 17	18
2.5 " "	7, 13, 15	—
2.6 " "	7, 12, 15	18
3.4 " "	13	—
3.5 " "	13	—
2 Methyl 6 Ethyl pyridine	12	18
2 " 4 " "	13	18
2 " 5 " "	16	18
4 " 3 " "	—	18
2.4 Diethyl pyridine	—	18
2.3.5 Trimethyl pyridine	13	—
2.3.6 " "	12	—
2.4.5 " "	13	—
2.4.6 " "	2, 4, 7, 8, 11, 16, 17	18
2.6 Dimethyl 4 Ethyl pyridine	13	—
2.3.4.6 Tetramethyl " "	13	—
Pyrindane (5.6 dihydro-pyrindene)	13	—
Quinoline	17	—
2 Methyl quinoline	17	—

In recent work at the Oil Shale Research and Development Laboratories of the U.S. Bureau of Mines (17) on the bases present in shale naphtha the ultra-violet absorption spectra, boiling points and refractive indices indicated the presence of quinoline and 2-methyl quinoline in different fractions. Since these bases have not been identified previously in shale oil this evidence cannot be taken as conclusive in the absence of chemical confirmation.

It would appear, therefore, that no quinoline bases have yet been identified beyond all reasonable doubt in shale oil, but this must not be taken to mean that they are not present.

ISOQUINOLINE BASES.

Robinson (21) and Robinson and Goodwin (22) examined the higher boiling bases from Scottish shale oil and reported that the bases belonged to the isoquinoline series. This classification was based entirely on the negative nature of the cyanine test which was quoted by a contemporary (23) as distinguishing between quinoline and isoquinoline bases. However, the cyanine test is valid only for 2 or 4 methyl quinolines and a negative test does not exclude quinoline itself. We can therefore say that these workers had no real evidence for classifying their bases as isoquinoline homologues.

As a point of interest it may be mentioned that the name "Tetracoline" which Robinson applied to his C_{12} base has been applied to 2,5,7 trimethyl quinoline (24), though this base does not appear to be listed in Beilstein.

McKee (2) remarked that "it is highly improbable that . . . isoquinolines and their hydroderivatives are present in more than very small amounts in the fractions of De Beque (Colorado) shale oil which boil below 300° C."

It is obvious, therefore, that no isoquinoline bases have yet been identified in shale oil, but this must not be taken to mean that they may not be present.

OTHER BASES.

It has been observed by the author that the carefully purified bases from cracked shale gasoline still contain as much as 0.2% of sulphur. From the method of purification employed (25) there was no neutral oil left in the bases, so the sulphur must have been present in the molecular structure of the bases. Thiazole bears the same relationship to the pyridine as does thiophene to benzene (e.g. pyridine b.p. 115° C., thiazole b.p. 117° C.) and is very similar in properties. It is therefore possible that thiazoles may be present in the bases, their similarity to the pyridines being a contributing factor to their having been overlooked. The 0.2% sulphur in the bases could be accounted for by the presence of approximately 1% of thiazoles.

SUMMARY.

The only organic nitrogen compounds that have been isolated and identified in shale oil are pyridine and its simple methyl and ethyl derivatives. The only bicyclic base isolated in pyridine in which the pyridine ring is fused to a cyclopentane ring. Quinoline and isoquinoline derivatives have been claimed but have not been identified with certainty.

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NITROGEN IN OIL SHALE AND SHALE OIL.

III. NITROGENOUS PRODUCTS FROM THE PYROLYSIS OF PORPHYRINS AND PROTEINS.

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INTRODUCTION.

In considering the possible forms of nitrogen compounds that may be present in shale oil the first step is to examine the primary decomposition products of the nitrogen compounds present in shale, and the second step is to examine the secondary reactions that can give rise to, modify, or destroy the bases.

In the first paper of this series (1) it was suggested that the nitrogenous constituents of shale kerogens are of porphyrinic and protein origin, and that the original chlorophyll and proteins have been modified by bacteriological action.

The pyrolytic decomposition of these two classes of compounds will be considered in turn and then the secondary reactions of the bases, etc., discussed in a later paper.

PYROLYSIS OF PORPHYRINS.

Apart from a few, controlled low temperature pyrolytic reactions in solution in connection with porphyrin syntheses, there appears to be no reference in the literature of the pyrolytic decomposition of porphyrins. The highest temperature that appears to have been used in porphyrin treatment was applied by Treibs (2). On slowly heating pheophytin in petroleum to 250°–320° C. he obtained phylloerythrin, and further heating to 360° C. gave desoxophylloerythro-ætioporphyrin.

Since the rate of thermal decomposition of kerogen is not appreciable below about 400° C., even higher temperatures than this must necessarily be used in retorting shale. Unfortunately no data is available on the stability of the porphyrin nucleus at such elevated temperatures, but the phthalocyanines, which have a similar structure, are stable.

An approximate calculation of the boiling point of dexosophylloerythro-ætioporphyrin using Nekrasov's formula for hydrocarbons (3) indicates that it would be well over 500° C. It is quite possible, however, that some of this porphyrin would distil, if sufficiently stable and thus appear in the crude shale oil.

Since the porphyrin molecule contains four substituted pyrrole nuclei it is a reasonable supposition that homologues of pyrrole will be among the products of thermal decomposition of porphyrins.

PYROLYSIS OF PROTEINS.

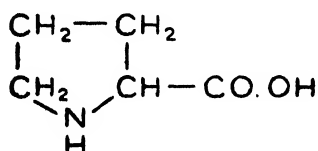
Ammonia is almost invariably present among the pyrolytic decomposition products of protein. It is also produced during the entire course of the pyrolysis of kerogen (4) though mainly at the higher temperatures (5). The condition by which the maximum yields of ammonia may be obtained from the shale have been the objects of many investigations (e.g. 5, 6, 7, 8, 9).

The greater proportion of the nitrogen in the kerogen always remains in combination in the residual coke from which it can be recovered in the form of ammonia by a current of steam (6, 8). Just as slow retorting of the shale increases the yield of ammonia at the expense of the residue, so does the use of high temperature increase the yield of ammonia at the expense of the nitrogenous constituents of the oil.

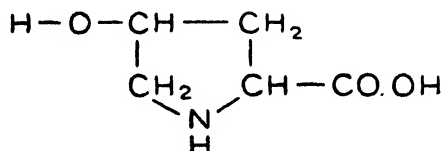
Of the amino acids occurring in proteins, proline (I) and hydroxyproline (II) both contain the hydrogenated pyrrole or pyrrolidine nucleus, and tryptophane (III) is a substituted indole (benzpyrrole).

The presence of indole among the pyrolytic decomposition products of proteins could be explained by the decomposition of tryptophane if present, while decarboxylation accompanied by dehydrogenation would convert proline and hydroxyproline into pyrrole. This, however, does not explain the origin of the pyrrole homologues in the shale oil, and these have been detected among

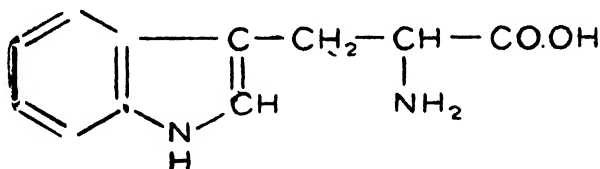
I. PROLINE



II. HYDROXYPROLINE.



III TRYPTOPHANE.



the higher tar bases (4, 10), of which they may constitute the greater portion. Among the products of the pyrolysis of silk fibroin Johnson and Daschavsky (11, 12) identified quinoline and indole. They isolated indole from the acid and caustic washed oil. Since silk fibroin does not contain tryptophane, it could not have come from this source and was probably formed by the decomposition of the trimer of pyrrole as described in the next paper of this series.

They suggested that the quinoline was formed by the pyrolysis of phenyl-alanine dipeptide residues which give rise to phenyl propionamide, which in turn was dehydrated, dehydrogenated and cyclized to quinoline. This purely theoretical mechanism for the reaction cannot be the full story, as the quinoline was formed by the decomposition of the alkali extract of the pyrolysis tar when attempts were made to purify it (12).

They also found that the acid extract of their oil possessed the odour of pyrrole. Pyrrole tests were always positive, but no treatment was found that enabled isolation of definite substances as they resinified rapidly in acid solution, and they oxidized and resinified on exposure to air.

Pictet and Cramer (12) distilled ovalbumin under reduced pressure and identified indole, several amides and a base which they tentatively considered to be a dihydroaniline, among the decomposition products.

Michelmann (14) observed that the pyrolysis of leather scrap gave an abundance of pyrocoll and pyrroles, and patented a process for the industrial

preparation of pyrroles by the destructive distillation of collagenous materials such as glue, gelatine and leather scrap (15). Meir (16) also utilized leather scrap for the production of pyrroles.

Domingues de Campo (17) detected pyrrole in the smoke of leaves which did not contain nicotine. In the light of the evidence presented here it seems probable that the pyrrole was formed from the proteins in the leaf.

As early as 1858 Anderson (18) isolated pyrrole in a pure condition from the so-called bone oil or Dippel's oil which was obtained by the destructive distillation of bones. Thorpe (19) listed ammonia, fatty acids, nitriles, pyrrole, pyridine, quinoline and their homologues and some primary amines and amides among the products of the destructive distillation of bones. The formation of these various products is considered to be due to the following reactions: decomposition of the protein matter to give pyrrole and its homologues, and ammonia; the formation of nitriles and amides by the action of the ammonia on the fats and fatty acids; and the formation of pyridine and its derivatives by the condensation of ammonia with acrolein from the decomposition of the glycerides.

Troensgaard and Mygind (20) demonstrated the presence of a pyridine nucleus in proteins by hydrogenating acetylated gliandin and casein with sodium in pyridine-free amyl alcohol, hydrolysing in the cold and fractionating the bases obtained. They thus isolated 0.25% of piperidine. They suggested, however, that the piperidine was obtained by the hydrogenation of a piperidone rather than a pyridine grouping.

Troensgaard (21) hydrogenated proteins in water-free media and examined the basic fractions after partial hydrolysis. He found some diketopiperazine rings had been hydrogenated to piperidine rings. Pyrrole rings were detected in some fractions, and piperidine was found in one hydrogenated protein.

No known naturally occurring amino acids from proteins contain a pyridine or piperidine nucleus, so pyridine homologues present in shale oil must have been produced by secondary reactions. However, cyclization of lysine (IV) or of arginine (V) would give rise to a piperidine nucleus. This same structure is present in the imide of glutamic acid (VI) but, in this case, pyridine alone would be obtained on decarboxylation and dehydrogenation.

IV. Lysine $\text{HN}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-CO}_2\text{H}$.

V. Arginine $\text{NH=C(NH}_2\text{)-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-CO}_2\text{H}$.

VI. Glutamic acid $\text{HO}_2\text{C-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-CO}_2\text{H}$.

It seems probable that the piperidine that Troensgaard obtained from the reduction of proteins was obtained by hydrogenation of the lactim of arginine after initial partial hydrolysis of the protein.

Carbonization of protein matter may, by promoting cyclization of these amino acids, give rise to pyridine, but not to its homologues. Only very small amounts of pyridine itself have been found among the bases in shale oil (22, 23, 24), so this mechanism does not seem to be of much importance even if it does occur.

Sibata and Sioya (25) found 7.3% by volume of pyridine type bases in the crude fuel oil obtained by the destructive distillation of sewage sludge. From the distillation range the basic oil was attributed to contain 34% quinoline, 18% collidine and about 5% pyridine. This observation of the formation of pyridine type bases is of interest because the nitrogenous constituents of the sewage sludge would be proteins which had been subjected to bacterial action, and would have had the opportunity to condense with aldehydes from the bacterial oxidation of carbohydrates, etc., to give heterocyclic nitrogen compounds as suggested by Maillard (26) in the formation of melanoids as an intermediate in coal formation.

Pictet and Chou (27) condensed casein with methylal in the presence of hydrochloric acid, dried the reaction product and distilled it with lime. They obtained a yellow oil which contained primary, secondary, and tertiary bases, from which they isolated and identified pyridine, 2,6 dimethyl pyridine, isoquinoline and 4 methyl isoquinoline. Several other bases were isolated and characterized but not identified. They were unable to detect the slightest trace of quinoline in the oil. In a control experiment without the addition of methylal none of the pyridine type bases was formed.

Maillard (28) also observed that the amino acids from protein hydrolysis condensed with aldehydes to give pyridine bases.

Parker, Gutzeit, Bratton and Bailey (29) distilled cotton seed meal with a nitrogen-free lubricating oil, which acted also as a liquid medium for control of the low temperature pyrolysis. They obtained 337 lb. of crude bases from 23 tons of the meal. At least 50% of the bases were insoluble in petroleum ether and they averaged more than one nitrogen atom per molecule. Also, the bases exhibited an exceptional tendency to tar formation. Pyridine and the following thirteen other bases containing the pyridine nucleus were isolated and identified.

2, 3, and 4 Methyl Pyridines.

3 Ethyl Pyridine.

2,4; 2,6: and 3,5: Dimethyl Pyridines.

2,4,6. Trimethyl Pyridine.

Quinoline and Isoquinoline.

Quinolidine and Lepidine.

2,3,8. Trimethyl Quinoline.

Another base which appeared to be an alkylated dihydroquinazoline was isolated and characterized but not identified. Pyrazines and pyrimidines were suspected but a search for diazines was fruitless.

Boisselt and Louis (30) carbonized solvent-extracted grape seeds and "marc" from the wine industry, and obtained ammonia and pyridine bases in the distillate amounting to approximately 0.4% by weight of the charge.

DISCUSSION.

On the basis of the evidence presented in this review it appears that the nitrogen compounds that may be present in shale oil are extremely varied. Thus pyrrole homologues and possibly porphyrins and their intermediate decomposition products can be expected from the porphyrins present in the kerogen. Proteins and modified proteins could give rise to pyrrole and pyrrole derivatives such as indole and pyrocoll, as well as to pyridine type bases including quinoline and isoquinoline, and to diazines, amides and nitriles. Ammonia liberated from protein material, etc., is very reactive at the high temperature involved in the retorting process, so secondary reactions involving the formation of heterocyclic nitrogen compounds must not be overlooked. Also, secondary reactions involving the modification and decomposition of the nitrogen compounds formed during the initial pyrolysis of the kerogen no doubt have a very important bearing on the nature and distribution of the nitrogen compounds present in the resultant crude oil. These reactions will be dealt with in a subsequent paper.

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NITROGEN IN OIL SHALE AND SHALE OIL.

IV. PYROLYTIC REACTIONS INVOLVING THE FORMATION AND DECOMPOSITION OF TAR BASES.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., M.Inst.Pet.

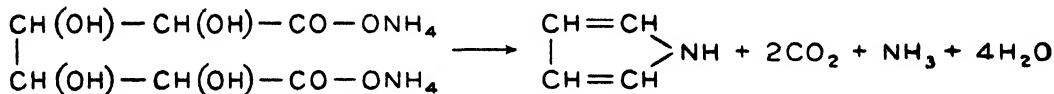
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A study of the simple homologues of the bases present in the shale oil is a help in understanding the reactions occurring during the pyrolysis of the kerogen and the subsequent refining of the oil.

Pyridine and pyrrole homologues have been detected in shale oil and pyrolytic reactions involving their formation and decomposition will be discussed. Although none have yet been detected in shale oil, heterocyclic nitrogen compounds with two or more hetero-atoms in the molecule may be present and are therefore included in the review.

SYNTHESIS OF PYRROLES.

Pyrrole itself can be synthesized by distilling the ammonium salt of mucic or saccharic acid (1, 2).



If monoalkylamines are used instead of ammonia in this synthesis N-alkyl pyrroles result (3, 4). On pyrolysis these readily rearrange to α alkyl pyrroles (5, 6, 7).

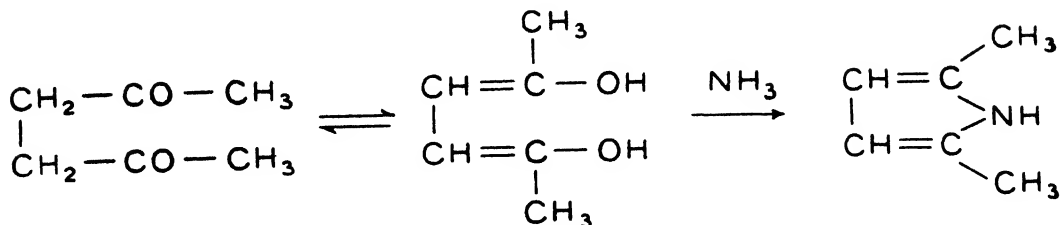
Pyrrole is also produced in small quantity by the action of heat on mixture of acetylene and ammonia (1, 8, 9, 10).

When butadiene and ammonia were passed over heated catalysts Schneider, Beck and Hausser (8) observed that the pyrrole ring was formed directly by ring closure without intermediate cleavage and with liberation of hydrogen, and that no materially greater amount of six, than of five membered ring compounds, were formed.

Pyrolysis of diethylamine gave rise to small yields of pyrrole (11, 12, 13) and N-ethyl aniline gave traces of indole (14) while N.N. dimethyl-o-toluidine gave relatively good yields of 1. methyl indole (15).

Since kerogen always contains an appreciable amount of oxygen, the presence of aldehydes and ketones in the crude shale oil is to be expected. γ di-ketones

readily condense with ammonia to give pyrroles even in the cold (1, 16, 17, 18). This is the Paal-Knorr reaction, e.g.



Carbohydrate materials such as cellulose are reported to be among the pregenitors of coal (19) and, as coal and shale are often claimed to have a similar origin, it may be possible that such materials constitute part of the kerogen. Furanes are formed during the pyrolysis of carbohydrates and it is probable that, by reaction with the ammonia that is produced during the pyrolysis of kerogen, pyrroles would be formed.

Shmook (20) obtained a product which gave the characteristic pine splinter reaction of pyrroles by heating glucose, starch or pentosans with ammonium salts. Better yields were obtained under reducing conditions. He also obtained a distillate which gave characteristic pyrrole reactions by passing ammonia through a boiling glycerine solution of glucose.

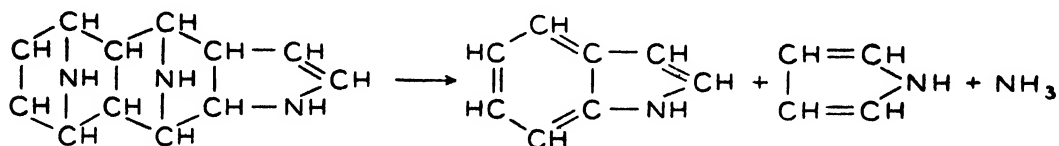
Wilson (21) passed ammonia and furan over activated alumina at 400° C. and identified pyrrole, pyrocoline, indole and carbazole in the products.

Yur'ev (22, 23) studied the reciprocal transformation of heterocyclic compounds with five-membered rings, and obtained yields of up to 40% of pyrrole by the treatment of furan with ammonia over an alumina catalyst at 550° C. The vapours of the product obtained by passing furfural and ammonia over alumina also gave an intense pine splinter reaction.

Graneli (24) obtained 2-methyl 3-ethyl pyrrole by passing 2,4 dimethyl pyridine and hydrogen over a nickel catalyst. However, this ring contraction does not seem to be likely to occur during shale carbonization.

PYROLYTIC REACTIONS OF PYRROLE WHICH RETAIN THE PYRROLE NUCLEUS.

Pyrroles polymerize extensively, particularly in the presence of acids, and the polymers do not depolymerize simply on heating but decompose to give a variety of products. The trimer of pyrrole is decomposed by heat to give pyrrole, ammonia and indole thus (1, 7, 25).



Similarly the dimer of ethyl pyrrole gives ammonia and diethyl indole on heating (7, 26).

Petrie (27) identified the deposit that formed in shale oil distillates on standing as a pyrrole polymer.

The crude secondary amines from shale oil are thermally unstable and decompose when distilled, even under vacuum, to give ammonia, free carbon and tertiary amines (28). It is logical to presume that the reaction involving the

evolution of ammonia is similar to the decomposition of tripyrrole. The formation of tertiary bases is almost certainly due to ring enlargement by α -alkyl groups as discussed later.

Skatole or β -methyl indole is readily demethylated to indole by heating, a reaction which can be realized by heating small amounts of skatole in a test-tube over a free flame (7, 29).

Pictet and Rilliet (30) observed that pyrrole readily condenses with formalin to give an insoluble, hard, dark red substance. In the presence of acid they obtained an insoluble white product which gave α methyl pyrrole when distilled alone.

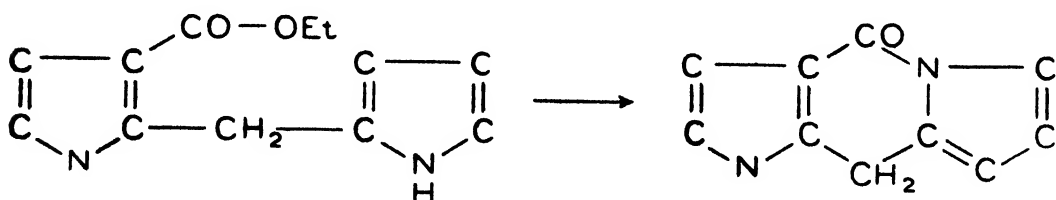
Backmann and Heisey (31) have isolated mono- and di- (amino-methyl) pyrroles from the tarry condensation products of pyrroles, secondary amines and formaldehyde. These products were unstable and decomposed on distillation.

Calvin *et al.* (32, 33) have identified $\alpha \beta \gamma \delta$ tetraphenyl porphine and the corresponding chlorin as the main condensation products of benzaldehyde and pyrrole.

These aldehydic condensation products of pyrrole indicate a possible mechanism by which the molecular weight of some of the nitrogenous constituents of shale oil could be increased to give fractions of boiling point higher than the retorting temperature.

From certain dipyrromethanes Corwin and co-workers (34, 35) have synthesized a new class of heterocyclic base, the dipyrrolo-pyridones. They remark, "Compounds of this new class have aroused interest in the laboratory because their colour and fluorescence in organic solvents markedly resemble those of crude oil. Since decomposition products of chlorophyll might conceivably be responsible for the fluorescence in crude oils and might also be related to these synthetic products, the possibility exists that analogues of these synthetic products occur in nature."

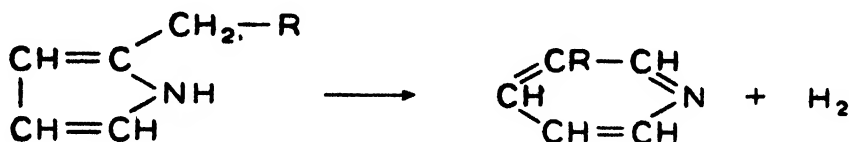
The new class of base is formed by the reaction :



Since chlorophyll degradation products are present in kerogen, it is quite conceivable that this class of base may be present in shale oil.

CONVERSION OF PYRROLES TO PYRIDINES.

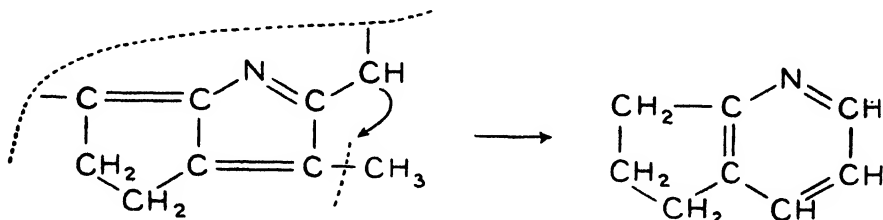
One of the characteristic pyrogenic reactions of α substituted pyrroles is the enlarging of the five-membered ring to a six-membered ring (e.g. 1, 5, 7, 36, 37), thus :



where "R" can be almost any radicle. Substitution of the pyrrole nucleus does not appear to interfere with the reaction. For example, fair yields of quinoline

were obtained by passing 2 methyl indole through a red hot tube (5, 37) and $\alpha\alpha$ dipyridyl was formed as a by-product during the pyrolytic formation of 2 (α pyridyl) 5-methyl pyrrole (6). Oddo (38) has recently reviewed and discussed the mechanism of this reaction.

The presence of pyrindane in shale oil (39) could quite possibly be due to the fission of a desoxoporphyrin in the kerogen followed by ring enlargement by the α bridge carbon atom, thus :



Putochin (40) obtained 4-methyl pyridine by passing pyrrole and hydrogen over nickel at 200° C. This reaction is obviously complicated and the products were probably formed by the recombination of the decomposition products of the pyrrole.

DECOMPOSITION OF THE PYRROLE NUCLEUS.

Literature on pyrolytic reactions involving the decomposition of the pyrrole nucleus is extremely scanty.

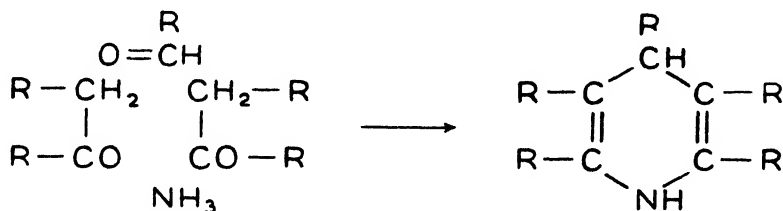
The formation and decomposition of tripyrrole, etc., as discussed earlier, does involve the decomposition of a pyrrole nucleus, but the formation of the indole is the main characteristic of the reaction.

Schneider, Beck and Hausser (8) observed that, on thermal catalytic decomposition pyrrole decomposed with the formation of hydrocarbons and they detected both hydrogen cyanide and ammonia among the products.

Woodward, Eisner and Haines (41) examined the pyrolytic decomposition products of nicotine. They obtained myosmine, nicotyrine, 2-methyl pyridine, 2-ethyl pyridine, 2-vinyl pyridine, pyridine, methylamine, ammonia and hydrogen cyanide among the products. These products indicated that the N-methyl pyrrolidine ring appears to be more susceptible to pyrogenic decomposition than the pyridine ring.

SYNTHESIS OF PYRIDINES.

The classical pyridine synthesis of Hantzsch (37) involves the condensation of aldehydes and/or ketones with ammonia to give a dihydro pyridine which is readily oxidized to the pyridine.



Since kerogen always contains an appreciable amount of oxygen, the presence of aldehydes and ketones in the crude oil is to be expected and a fair proportion of them will condense with ammonia during the pyrolysis of the kerogen and any

subsequent distillation. Horne, Finley and Hopkins (28) found that aldehydes and ketones in crude shale oil could be accounted for after distillation only as tertiary amines.

From the condensation products of acetaldehyde and ammonia Tschitschibabin (43) isolated and identified α and γ picoline, β collidine, aldehyde collidine, α and β propyl pyridines and a small amount of α propenyl pyridine. Propionaldehyde and ammonia yielded 2- and 4-ethyl 3,5, dimethyl pyridines, while crotonaldehyde and ammonia gave 3-ethyl 4-methyl pyridine (44). β picoline may be obtained by the dry distillation of acrolein ammonia (45) or by the passage of acrolein and ammonia over aluminium phosphate at 350° C. (46).

Pyridine and pyridine derivatives are among the products of dry distillation of bones (1, 47). If the fat is removed from the bones prior to carbonization, no pyridine derivatives are formed, while free fatty acids are converted to their nitriles. The formation of pyridine bases in bone oil therefore depends on the presence of the glycerol which is dehydrated at high temperature to acrolein. This apparently condenses with ammonia formed from the protein matter to give the pyridine bases.

α picoline may be obtained by autoclaving ammonia, formalin and paraldehyde at 110° C. (48, 49) and the use of the other aldehydes and/or ketones gives corresponding complex mixtures.

Pictet and Stehlin (5) noted that ketones and amides can be condensed to pyridines by heat alone. Thus acetone and acetamide heated in a sealed tube at 250° C. gave a 2-3% yield of 2,4,6 trimethyl pyridine, while paraldehyde and acetamide gave a small yield of α picoline. Pyridine and other products were obtained by passing ethanol and ammonia over red hot iron (51). Similar results have been obtained with the higher alcohols and ammonia using zinc oxide catalyst at high temperatures (52). It has been suggested that aldehydes may be formed as intermediates (53).

Small yields of acetylene are obtained by the pyrolysis or partial combustion (54) of hydrocarbons. The high temperature condensation products of ammonia and acetylene have been studied rather extensively and pyridine derivatives have been isolated and identified among the products. Aldehyde ammonia appears to be an important intermediate in the condensation and has been isolated from the reaction mixture (8, 9, 55). Products isolated and identified from the ammonolysis of acetylene are listed in Table 1.

By condensation of methylamine and acetylene at 300° C. over zinc bromide-pumice catalyst Nicodemus and Schmidt obtained a product containing 25-30% pyridine and 50-60% of pyridine homologues (56).

In 1877 Ramsay (57) observed the formation of pyridine by the pyrolytic condensation of acetylene and hydrogen cyanide, a reaction which is analogous to the thermal polymerization of acetylene to benzene. Meyer and Wesche have (10) identified pyrrole, pyridine, quinoline and benzonitrile among the products of this reaction.

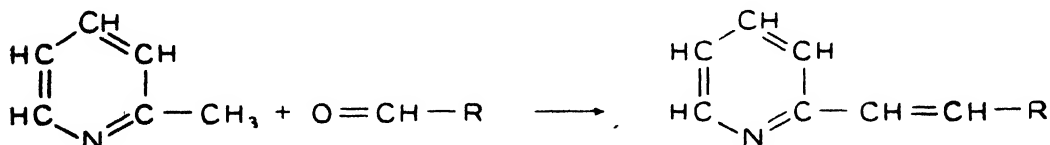
Tschitschibabin (13) has also obtained pyridine bases by the condensation of ammonia and ethylene over an alumina catalyst.

Small yields of pyridine bases have been obtained by heating ammonium bases or salts with glucose (58) or glycerol (59, 60, 61).

Kline and Turkevich (11) examined a number of possible pyrolytic syntheses of pyridine and obtained mixtures of pyridine and piperidine from ammonia and tetra-hydrofurfuryl alcohol, dihydropyran and pentamethylene oxide at temperatures in the vicinity of 400° C.

REACTIONS OF PYRIDINE WHICH RETAIN THE PYRIDINE NUCLEUS.

Pyridine bases which have a methylene group in the α or γ position show exceptional reactivity and condense readily with aldehydes. The mechanism of this reaction has recently been discussed by Roberts (62).



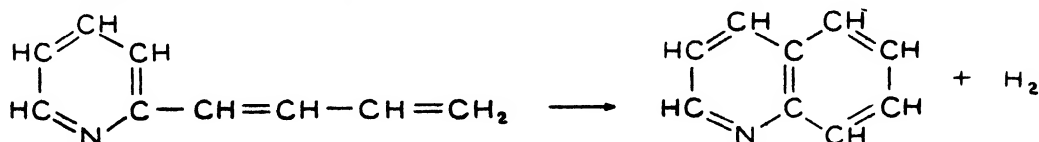
In this manner high boiling pyridine homologues would be formed from lower boiling materials.

TABLE 1.
Products of the Condensation of Ammonia and Acetylene.

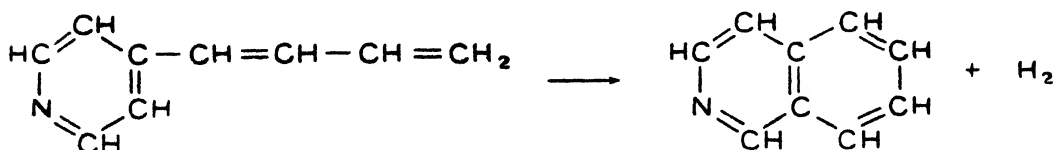
Products.	Reference.
Pyridine	10, 87
2 Picoline	9, 55, 88
3 Picoline	9, 55
4 Picoline	89, 90
1.4 Dimethyl pyridine	89, 90
2 Methyl 3 Ethyl pyridine	9
2 Methyl 5 Ethyl pyridine	9, 55
3 Methyl 4 Ethyl pyridine	55, 89, 90
2.3.6. Trimethyl pyridine	55
Indole	10
Pyrrole	1, 8, 9, 10
Quinoline	10
Aldehyde ammonia	8, 9, 55
Monoethylamine	55, 91, 92
Diethylamine	91, 92
Triethylamine	92
Aniline	10
Acetonitrile	9, 93
Benzonitrile	10

It must also be remembered that the nature of the side chains present in the high molecular weight bases will have an important bearing on the nature of the products of pyrolysis.

If the position adjacent to a long chain substituent is vacant it is conceivable that quinolines or isoquinolines could be formed by ring closure. Thus the condensation product of acrolein and α picoline could cyclise to quinoline.



Similarly γ picoline could give isoquinoline.



This suggests that benz-pyridines, which are yet to be identified for certainty in shale oil, could be derived from the simpler pyridines by secondary reactions.

On heating N-alkyl pyridinium compounds in a sealed tube to about 300° C. the alkyl group migrates to the α or γ position in the ring to give substituted pyridines (e.g. 1, 7, 63, 64, 65). This reaction is similar to the Hoffmann-Martius rearrangement, the mechanism of which is still in dispute, although recent evidence shows that the reaction involves the formation of free radicals. The voluminous literature now appearing on the mechanism of the cracking of hydrocarbons (e.g. 66, 67, 68) has shown beyond doubt that acceptance of radicle formation is necessary to explain the results. Shale carbonization involves the cracking of the kerogen to obtain the crude oil, so alkylation of pyridine homologues during the process may well take place.

If pyridine vapour is passed through a red hot tube dipyrityls are formed in a manner analogous to the formation of diphenyl from benzene. Of the six possible isomers the 44' isomer is the only one that has not been identified in the condensation products which also contains some tripyridyls (1). Similarly α picoline gives dipicolyls, lutidines yield dilutidyls, collidines yield dicollidyls and quinoline yields diquinolyls (7). By extending this reaction it is possible to conceive the formation of very high molecular weight materials containing pyridine nuclei. Also, pyrolysis of nicotinic acid gives small yields of $\beta\beta'$ dipyrityl ketone (69).

DECOMPOSITION OF THE PYRIDINE NUCLEUS.

References in the literature to the pyrolytic decomposition of the pyridine nucleus are extremely few. This is no doubt due to the fact that, although the free energy of formation of pyridine from the elements is positive and increases with temperature (11) the simplest decomposition mechanism, involving the formation of vinyl acetylene and hydrogen cyanide, also has a high positive free energy (70).

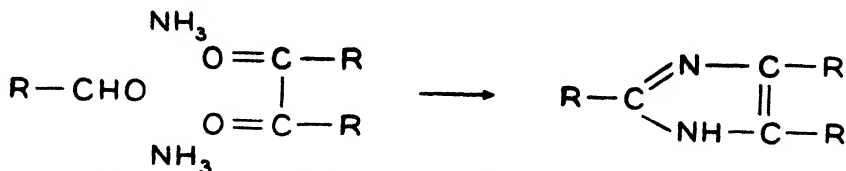
The author has observed hydrogen cyanide corrosion by the products from the cracking of crude shale oil, which contains pyridine homologues along with other nitrogen compounds (70).

On cracking the pyridine bases from brown coal tar Ruhemann (71) obtained from 6% to 7% by weight of hydrogen cyanide as well as some dipyrityls.

FIVE-MEMBERED RINGS WITH TWO NITROGEN ATOMS.

Pyrazoles are not very likely to be formed in the shale kerogen or during its pyrolytic decomposition as they are cyclic hydrazine derivatives. Pyrazole itself is stable to 300° C. but related compounds are less stable, thus N-phenyl-pyrazole melts with decomposition at 178° C. (7). The dihydropyrazoles or pyrazolines are unstable and decompose on heating to give cyclopropane derivatives (72).

The imidazoles or glyoxalines are formed by the condensation of ammonia and aldehydes with 1.2 diketones (72), thus:

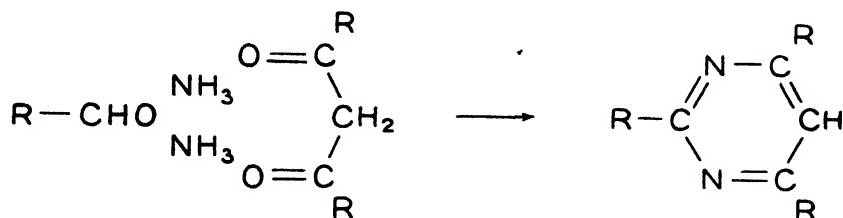


There is a scarcity of data available regarding the thermal stability of these compounds, but imidazole itself boils at 256° C. (74) and it is reported that the passage of N-methyl imidazole through a red hot tube causes rearrangement to C-methyl iminazole (7, 75).

SIX-MEMBERED RINGS WITH TWO NITROGEN ATOMS.

Pyridazines, like pyrazoles, are cyclic hydrazine derivatives and it is therefore most unlikely that this ring structure would be present in shale kerogen or formed during its pyrolytic decomposition. They will therefore not be discussed further.

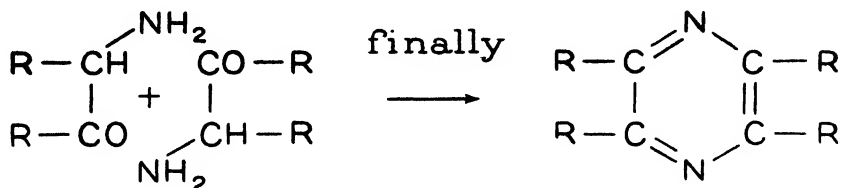
Substituted pyrimidines may be obtained by the pyrolysis of proteins (76) or by the condensation of ammonia and an aldehyde with β diketones, thus :



The condensation of acetone and ammonia in the presence of ammonium salts yields 2.2.4.6.6. pentamethyl 1.2.5.6. tetrahydro pyrimidine (77). It was suggested that pyrolysis of this compound would split off methane from the gem dimethyl groups to give the trimethyl pyrimidine. Uracil or dihydroxy pyrimidine is an essential constituent of some nucleic acids as are some substituted purines which contain the pyrimidine and imidazole rings fused together. It is therefore possible that small amounts of these structures may be present in shale kerogen or its decomposition products. Uric acid, which is trihydroxy purine gives urea, hydrogen cyanide, cyanuric acid and carbon on dry distillation (78, 79).

Pyrazines occur in the fermentation products of sugar. Thus $\alpha\gamma$ dimethyl and trimethyl pyrazines have been isolated from fusel oil (61). The chief constituent of the bases produced by the action of ammonia on glucose is methyl pyrazine (61), pyrazine and dimethyl pyrazines being formed at the same time. $\alpha\gamma$ dimethyl pyrazine is formed together with pyridine bases and other alkyl pyrazines, e.g. α methyl $\gamma\delta$ diethyl pyrazine, upon distilling glycerol with ammonium salts (61).

Pyrazines are also formed by the condensation of two molecules of α amino-aldehydes or ketones, the intermediate dihydro pyrazine being readily oxidized to the pyrazine by atmospheric oxygen (80).



The pyrazine nucleus appears to be reasonably heat stable as tetraphenyl pyrazine, which melts at 246°C ., sublimes without decomposition (74).

RINGS CONTAINING NITROGEN AND ANOTHER HETERO ATOM.

By condensing acetylene with ammonia and hydrogen sulphide or sulphur Nicodemus (81) obtained a product which consisted largely of thiophene together with alkyl thiophenes, mercaptans, pyridine homologues and some materials which contained both nitrogen and sulphur. The structure of these latter

materials was not determined but they were partly thiocyanate and partly basic in character. Since diketotetrahydrothiazole is obtained by the evaporation of thiocyanacetic acid with acids (82) it appears likely that the basic portion of these nitrogen and sulphur containing materials are thiazoles.

It is possible that oxazoles could be formed in an analogous manner, but the principal effect of adding steam instead of hydrogen sulphide to the reactants was to greatly increase the yield of pyridine bases (83). Pyrroles are more stable than the furans but less stable than the thiophenes (84). Since oxazoles and thiazoles have the same relationship to one another as have furans and thiophenes, it appears that, although thiazoles may be obtained, the formation of oxazoles is much less certain.

Also, isoxazoles and the corresponding isothiazoles are not considered as likely to be present in the shale kerogen or shale oil as they are substituted hydroxylamines.

The six-membered ring compounds containing nitrogen and another heterocyclic atom are much less well known than their five-membered ring analogues with perhaps the exception of phenthiazine and phenoxazine. The former is, normally prepared by heating diphenylamine with sulphur, but no pyrolytic preparation of the latter appears to have been used.

The two fused benzene rings can be expected to stabilize the structure of the heterocyclic ring, but phenthiazine boils with decomposition at 371° C. (74). In view of the relatively greater thermal stability of the five-membered than the six-membered ring structure containing an oxygen or sulphur atom it seems likely that the most probable representatives of this group to be found in shale oil are the thiazoles.

COMPOUNDS WITH MORE THAN TWO HETERO ATOMS.

It is considered that the only compounds containing more than two hetero atoms in the ring that warrant consideration in this discussion are cyanuric acid and its derivatives. On destructive distillation cyanuric acid (m.p. 360° C. (74)) and its esters decompose to cyanic acid (85).

Kirner (85) lists cyanuric acid among the nitrogenous products isolated from soil humus, humic acid preparations and peat, so it may also be present in shale kerogen in small amounts. Destructive distillation of cyanuric acid or its esters (86) yields cyanic acid, which can repolymerize to give some cyanuric acid in the distillate. In this manner both cyanic and cyanuric acid may be present in small amounts in shale oil.

SUMMARY.

From this review of the secondary pyrolytic reactions that could take place during the retorting of oil shale it is apparent that a wide range of cyclic nitrogen compounds may be present in shale oil. These include pyrrole and pyridine, their homologues and benz-derivatives, together with materials which contain more than one heterocyclic ring. Diheterocyclic compounds also may be formed though, for stability, the two hetero atoms should not be adjacent. It is also possible that non-cyclic, non-basic nitrogenous compounds such as nitriles and thiocyanates may be present.

Decomposition of the bases formed may influence the products appreciably, thus pyrroles can give rise to indoles and ammonia while pyridines would tend to give mainly dipyridyls with a small amount of nuclear decomposition to give hydrocarbons and hydrogen cyanide.

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ELECTRO-MAGNETO-IONIC OPTICS.

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1. INTRODUCTION.

The study of electric waves emitted under certain conditions by discharge tubes, by the Ionosphere and the Solar Atmosphere, has not hitherto been accompanied by a theory, based on Maxwell's equations, which takes account of the effects which may be due to static electric fields.

It is proposed here to give the fundamental set of equations from which such a theory may be developed. The main restriction involved in this set is that the motion of the positive ions is neglected.¹

The essential problem to be considered is to determine the electric waves which can exist in a medium consisting of electrons (N_0 per cc.), positive ions (N_i per cc.) and molecules (or atoms) and subject to static electric and magnetic fields (E_0 and H_0 respectively).

A preliminary note on this work has been published² in *Nature*.

2. NOTATION.³

The principal notation to be used is given in the following table, where the static values of the variables are indicated by means of a subscript 0 .

e, m =electron charge and mass respectively, in e.s.u.

N, N_i =electron and positive ion densities respectively.

U =mean velocity of the electrons.

E, H =electric vector (e.s.u.) and magnetic vector (e.m.u.) respectively.

A, V =vector and scalar potentials respectively.

ω, ν =wave angular frequency and electron collision frequency respectively.

q^{-1}, λ =wave-velocity and wave-length respectively.

r, ζ defined by : $r=1-q U_1, \zeta=c^2q^2-1$, where U_1 is the x -component of U_0 the drift-velocity.

$p_0 = \sqrt{4\pi N_0 e^2/m} = 5.65 \times 10^4 \sqrt{N_0}$.

$\tilde{\Omega}_0 = (-e/mc) H_0$ =the gyro-frequency vector.

T =mean kinetic energy of an electron.

p =partial pressure of the electrons = $\frac{2}{3} N T$.

$\tau = 2T/3m$.

i, j, k =orthogonal unit vectors, parallel to the x, y and z axes respectively.

¹ This restriction will be removed in a later publication.

² *Nature*, 161, April 17, 1948.

³ All Clarendon type and the symbol $\tilde{\Omega}_0$ indicate vectors.

$$\begin{aligned}\check{\nabla} &= \mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \\ D_t &= \frac{\partial}{\partial t} \\ \square^2 &= \nabla^2 - c^{-2} D_t^2 \\ D &= \frac{\partial}{\partial t} + (\mathbf{U} \check{\nabla}), & D_0 &= \frac{\partial}{\partial t} + (\mathbf{U}_0 \check{\nabla}). \\ c &= \text{velocity of light in vacuo.}\end{aligned}$$

The components of any vector \mathbf{U}_0 or \mathbf{u} are denoted by U_1, U_2, U_3 or u_1, u_2, u_3 and the components transverse to the x -axis are denoted by \mathbf{U}_T or \mathbf{u}_T .

3. THE FUNDAMENTAL EQUATIONS.

The fundamental relations between the six variables $N, \mathbf{U}, \mathbf{E}, \mathbf{H}, \mathbf{A}, V$ are as follows (when the motion of the positive ions is neglected).

$$D_t V = -c \check{\nabla} \mathbf{A}, \quad \dots \dots \dots (1)$$

$$\mathbf{E} = -c^{-1} D_t \mathbf{A} - \check{\nabla} V, \quad \dots \dots \dots (2)$$

$$\mathbf{H} = \check{\nabla} \times \mathbf{A}, \quad \dots \dots \dots (3)$$

$$4\pi e c^{-1} N \mathbf{U} = -\square^2 \mathbf{A}, \quad \dots \dots \dots (4)$$

$$4\pi e (N - Ni) = -\square^2 V, \quad \dots \dots \dots (5)$$

$$D \mathbf{U} + \nu \mathbf{U} = (e/m)(\mathbf{E} + c^{-1} \mathbf{U} \times \mathbf{H}) - N^{-1} \check{\nabla} \tau N \quad \dots \dots \dots (6)$$

The relation (6) is derivable from Maxwell's theory of transport of momentum.¹

It can also be derived in the following simple way.

A group of N electrons with a mean momentum $Nm\mathbf{U}$ will lose this momentum at the rate $\nu(Nm\mathbf{U})$ where ν is a constant which depends on the total number of other particles present per cc.; ν will be called the average collision frequency of an electron.

If \mathbf{F} is the intensity of the electromagnetic force on an electron, i.e.

$$\mathbf{F} = \mathbf{E} + c^{-1} \mathbf{U} \times \mathbf{H},$$

and p is the partial pressure of the electrons, therefore

$$mN \frac{d\mathbf{U}}{dt} = Ne\mathbf{F} - \text{grad } p - \nu Nm\mathbf{U}. \quad \dots \dots \dots (7)$$

Since $p = \tau m N$, (7) reduces to (6).

It is shown in the Appendix that (6) is consistent with the classical formulae of J. S. Townsend for the steady motions of electrons under the action of uniform static electric and magnetic fields.

From (1) to (6) we obtain the following relations between the static quantities $N_0, \mathbf{U}_0, \mathbf{E}_0, \mathbf{H}_0, \mathbf{A}_0, V_0$.

$$0 = -c \check{\nabla} \mathbf{A}_0, \quad \dots \dots \dots (1.0)$$

$$\mathbf{E}_0 = -\check{\nabla} V_0, \quad \dots \dots \dots (2.0)$$

$$\mathbf{H}_0 = \check{\nabla} \times \mathbf{A}_0, \quad \dots \dots \dots (3.0)$$

$$4\pi e c^{-1} N_0 \mathbf{U}_0 = -\square^2 \mathbf{A}_0, \quad \dots \dots \dots (4.0)$$

$$4\pi e (N_0 - Ni) = -\square^2 V_0, \quad \dots \dots \dots (5.0)$$

$$D_0 \mathbf{U}_0 + \nu \mathbf{U}_0 = (e/m)(\mathbf{E}_0 + c^{-1} \mathbf{U}_0 \times \mathbf{H}_0) - N_0^{-1} \check{\nabla} \tau N_0 \quad \dots \dots (6.0)$$

¹ J. C. Maxwell, "Scientific Papers", Vol. 2, pp. 51-58. (Camb. Univ. Press, 1890.)

We now set

$$\left. \begin{aligned} N &= N_0 + n, & \mathbf{U} &= \mathbf{U}_0 + \mathbf{u}, \\ \mathbf{E} &= \mathbf{E}_0 + \mathbf{e}, & \mathbf{H} &= \mathbf{H}_0 + \mathbf{h}, \\ \mathbf{A} &= \mathbf{A}_0 + \mathbf{a}, & \mathbf{V} &= \mathbf{V}_0 + \mathbf{v}, \end{aligned} \right\} \dots\dots\dots (8)$$

and for a first approximation take n , \mathbf{u} , \mathbf{e} , \mathbf{h} , \mathbf{a} , \mathbf{v} as relatively small periodic quantities of a common frequency.

On subtracting (1.0) from (1), (2.0) from (2), etc., using (8) and retaining only terms linear in n , \mathbf{u} , \mathbf{e} , etc., the following system of differential equations is obtained for a medium which is uniform when in the static state :

$$D_t \mathbf{v} = -c \nabla \mathbf{a}, \dots\dots\dots (1.1)$$

$$\mathbf{e} = -c^{-1} D_t \mathbf{a} - \nabla v, \dots\dots\dots (2.1)$$

$$\mathbf{h} = \nabla \times \mathbf{a}, \dots\dots\dots (3.1)$$

$$N_0 \mathbf{u} + \mathbf{U}_0 n = -(e/4\pi e) \square^2 \mathbf{a}, \dots\dots\dots (4.1)$$

$$n = -(1/4\pi e) \square^2 v, \dots\dots\dots (5.1)$$

$$D_0 \mathbf{u} + \mathbf{v} \mathbf{u} = (e/m) \mathbf{e} + \tilde{\Omega}_0 \times \mathbf{u} + (e/mc) \mathbf{U}_0 \times \mathbf{h} - \tau \nabla (n/N_0) \dots\dots (6.1)$$

When the medium in the static state is not uniform (6.1) must be supplemented by additional terms.

On eliminating \mathbf{e} , \mathbf{h} , \mathbf{u} and n between these equations we are left with (1.1) and the following equation in \mathbf{a} and v :

$$(D_0 + v - \tilde{\Omega}_0 \times) [-\mathbf{U}_0 \square^2 v + c \square^2 \mathbf{a}] = -p_0^2 \mathbf{f} - \tau \nabla \square^2 v \dots\dots\dots (9)$$

where

$$\mathbf{f} = -c^{-1} D_t \mathbf{a} - \nabla v + c^{-1} \mathbf{U}_0 \times (\nabla \times \mathbf{a}) \dots\dots\dots (10)$$

(1.1) and (9) can be solved for \mathbf{a} and v .

4. EQUATIONS FOR PLANE WAVES.

The solutions for plane waves propagated along the x -axis of rectangular coordinates are found by taking all the variables as proportional to

$$e^{i\omega(t-qx)}$$

where in general ω and q may be complex numbers.

The corresponding physical quantities will be taken as the real parts of the variables.

We may here now set

$$\left. \begin{aligned} D_t &= i\omega, & D_0 &= i\omega r, \\ \nabla &= -i\omega q \mathbf{i}, & \square^2 &= -\omega^2 c^{-2} \zeta, \end{aligned} \right\} \dots\dots\dots (11)$$

where

$$r = 1 - q U_1, \quad \zeta = c^2 q^2 - 1. \dots\dots\dots (12)$$

Then (1.1) becomes

$$v = c q a_1, \dots\dots\dots (13)$$

and so from (9) we obtain

$$\begin{aligned} &(\delta - \tilde{\Omega}_0 \times)(r \mathbf{a}_1 + \mathbf{a}_T - q U_T \mathbf{a}_1) \\ &= i\omega_0 \{ \mathbf{a}_1 - \zeta^{-1} r \mathbf{a}_T - \zeta^{-1} q U_T \times (\mathbf{i} \times \mathbf{a}_T) \} + i\tau \omega q^2 \mathbf{a}_1, \dots\dots\dots (14) \end{aligned}$$

where

$$\delta = v + i\omega r, \dots\dots\dots (15)$$

$$\omega_0 = p_0^2 \omega^{-1}. \dots\dots\dots (16)$$

As a check we find that when $U_0=0$ and $\tau=0$ (14) reduces to

$$(\nu + i\omega + i\omega_0\zeta^{-1})\mathbf{a} - i\omega_0(1 + \zeta^{-1})\mathbf{a}_1 - \tilde{\Omega}_0 \times \mathbf{a} = 0$$

which agrees, as it should, with equation (13) in a previous publication.¹

5. SOLUTIONS OF THE EQUATIONS FOR PLANE WAVES.

On setting in (14)

$$\begin{aligned}\mathbf{a} &= a_1\mathbf{i} + a_2\mathbf{j} + a_3\mathbf{k}, \\ \mathbf{U}_0 &= U_1\mathbf{i} + U_2\mathbf{j} + U_3\mathbf{k}, \\ \tilde{\Omega}_0 &= \Omega_1\mathbf{i} + \Omega_2\mathbf{j} + \Omega_3\mathbf{k},\end{aligned}$$

and equating coefficients of \mathbf{i} , \mathbf{j} and \mathbf{k} on both sides we obtain the following system of simultaneous equations in a_1 , a_2 , a_3 .

$$\left. \begin{aligned}\alpha_1 a_1 + \alpha_2 a_2 + \alpha_3 a_3 &= 0, \\ \beta_1 a_1 + \beta_2 a_2 + \beta_3 a_3 &= 0, \\ \gamma_1 a_1 + \gamma_2 a_2 + \gamma_3 a_3 &= 0,\end{aligned} \right\} \dots\dots\dots (17)$$

where

$$\left. \begin{aligned}\alpha_1 &= \nu + i\psi - qb_1, & \alpha_2 &= \Omega_3 + igU_2, & \alpha_3 &= -\Omega_2 + igU_3, \\ \beta_1 &= -\Omega_3 - qb_2, & \beta_2 &= \xi, & \beta_3 &= \Omega_1, \\ \gamma_1 &= \Omega_2 - qb_3, & \gamma_2 &= -\Omega_1, & \gamma_3 &= \xi\end{aligned} \right\} \dots\dots\dots (18)$$

$$\left. \begin{aligned}\psi &= \omega r - \omega_0 - \tau\omega q^2, \\ \xi &= \nu + ir(\omega + \omega_0\zeta^{-1}),\end{aligned} \right\} \dots\dots\dots (19)$$

$$\left. \begin{aligned}b_1 &= \delta U_1 + \Omega_3 U_2 - \Omega_2 U_3, \\ b_2 &= \delta U_2 + \Omega_1 U_3 - \Omega_3 U_1, \\ b_3 &= \delta U_3 + \Omega_2 U_1 - \Omega_1 U_2,\end{aligned} \right\} \dots\dots\dots (20)$$

$$g = \omega_0 q \zeta^{-1}. \dots\dots\dots (21)$$

If

$$\Delta = \begin{vmatrix} \alpha_1 & \alpha_2 & \alpha_3 \\ \beta_1 & \beta_2 & \beta_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{vmatrix} \dots\dots\dots (22)$$

and α' , α'' , α''' are the cofactors of α_1 , α_2 , α_3 respectively, then the necessary and sufficient condition for (17) to have a finite solution is that

$$\Delta = 0, \dots\dots\dots (23.1)$$

and the solution is then given by

$$a_1 = C\alpha', \quad a_2 = C\alpha'', \quad a_3 = C\alpha''',$$

i.e. by

$$\left. \begin{aligned}a_1 &= C(\xi^2 + \Omega_1^2), \\ a_2 &= C[\xi(\Omega_3 + qb_2) + \Omega_1(\Omega_2 - qb_3)], \\ a_3 &= C[\xi(-\Omega_2 + qb_3) + \Omega_1(\Omega_3 + qb_2)].\end{aligned} \right\} \dots\dots\dots (24.1)$$

From this we have

$$a_T = \sqrt{a_2^2 + a_3^2} = C\sqrt{(\xi^2 + \Omega_1^2)T}$$

where

$$T = (\Omega_3 + qb_2)^2 + (\Omega_2 - qb_3)^2.$$

On expanding T and using (20) we obtain eventually

$$T = \Omega_T^2 r^2 + 2\Omega_T U_T q r (\delta \sin \theta + \Omega_1 \cos \theta) + U_T^2 q^2 (\delta^2 + \Omega_1^2),$$

where θ is the angle between \mathbf{H}_T and \mathbf{U}_T .

¹ V. A. Bailey, *Phil. Mag.*, 23, p. 929 (1937).

Accordingly from (24.1) we obtain

$$\left. \begin{aligned} a_1 &= C\chi\sqrt{\xi^2 + \Omega_1^2}, \quad a_2 = a_T \cos \varphi, \quad a_3 = a_T \sin \varphi \\ \text{where} \quad a_T &= C\chi\sqrt{r^2\Omega_T^2 + 2arg\Omega_T U_T + bq^2 U_T^2}, \\ a &= \delta \sin \theta + \Omega_1 \cos \theta, \\ b &= \delta^2 + \Omega_1^2, \end{aligned} \right\} \dots\dots (24.2)$$

C is an arbitrary constant, φ is the "angle" between a_T and the y -axis and $\chi = e^{i\omega(t-qx)}$.

From (18) we have

$$\left. \begin{aligned} \alpha_1 &= \rho_1 + i\rho_2, \\ \beta_1 &= \sigma_1 + i\sigma_2, \\ \gamma_1 &= \tau_1 + i\tau_2, \end{aligned} \right\} \dots\dots\dots (25)$$

where

$$\left. \begin{aligned} \rho_1 &= vr - q(\Omega_3 U_2 - \Omega_2 U_3), & \rho_2 &= \omega r^2 - \omega_0 - \tau\omega q^2, \\ \sigma_1 &= -\Omega_3 r - q(v U_2 + \Omega_1 U_3), & \sigma_2 &= -\omega r q U_2, \\ \tau_1 &= \Omega_2 r - q(v U_3 - \Omega_1 U_2), & \tau_2 &= -\omega r q U_3. \end{aligned} \right\} \dots\dots (26)$$

On adding to the first column of Δ , qU_2 times the second column and qU_3 times the third column we obtain

$$\Delta = \begin{vmatrix} \alpha & \alpha_2 & \alpha_3 \\ \beta & \beta_2 & \beta_3 \\ \gamma & \gamma_2 & \gamma_3 \end{vmatrix} \times r \dots\dots\dots (27)$$

where

$$\begin{aligned} \alpha r &= \alpha_1 + \alpha_2 q U_2 + \alpha_3 q U_3, \\ \beta r &= \beta_1 + \beta_2 q U_2 + \beta_3 q U_3, \\ \gamma r &= \gamma_1 + \gamma_2 q U_2 + \gamma_3 q U_3. \end{aligned}$$

On using (18), (25) and (26) we find that

$$\left. \begin{aligned} \alpha &= v + i(\omega r - p_0^2 \omega^{-1} r^{-1} s - \tau\omega q^2 r^{-1}), \\ \beta &= -\Omega_3 + ig U_2, \\ \gamma &= \Omega_2 + ig U_3, \end{aligned} \right\} \dots\dots\dots (28)$$

where

$$s = 1 - \zeta^{-1} q^2 U_T^2. \dots\dots\dots (29)$$

From (27) and (28) we now obtain

$$\Delta = \alpha(\xi^2 + \Omega_1^2)r + \xi(\Omega_T^2 + g^2 U_T^2)r + 2ig\Omega_1(\Omega_2 U_2 + \Omega_3 U_3)r \dots (27.1)$$

where

$$\xi = v + i(\omega r + p_0^2 \omega^{-1} \zeta^{-1} r). \dots\dots\dots (30)$$

Hence the condition (23.1) becomes

$$r\alpha(\xi^2 + \Omega_1^2) + r\xi(\Omega_T^2 + g^2 U_T^2) + irg U_T s = 0 \dots\dots\dots (23.2)$$

where

$$\left. \begin{aligned} S &= 2\Omega_1 \Omega_T \cos \theta, \\ \theta &= \text{angle between } H_T \text{ and } U_T. \end{aligned} \right\} \dots\dots\dots (31)$$

On multiplying (23.2) throughout by $i\omega^3 \zeta^2$ it becomes

$$\begin{aligned} &[\omega^2(r^2 - \tau q^2) - p_0^2 + p_0^2 \zeta^{-1} q^2 U_T^2 - i\omega r v] [(\omega^2 \zeta r + p_0^2 r - i\omega v \zeta)^2 - \Omega_1^2 \omega^2 \zeta^2] \\ &\quad - (\omega^2 r^2 + p_0^2 r^2 \zeta^{-1} - i\omega r v)(\Omega_T^2 \omega^2 \zeta^2 + p_0^4 q^2 U_T^2) \\ &\quad - p_0^2 \omega^2 r \zeta q U_T s = 0. \dots\dots\dots (23.3) \end{aligned}$$

The terms in (23.3) which contain ζ^{-1} mutually cancel. Hence (23.3) contains only positive powers of ω and ζ . It is of the 6th degree in ω and of the 8th degree in q .

On dividing throughout by p_0^6 and setting

$$\frac{\omega}{p_0} = w, \quad \frac{\Omega_1}{p_0} = W_1, \quad \frac{\Omega_T}{p_0} = W_T, \quad \frac{\Omega_0}{p_0} = W_0, \quad \frac{\nu}{p_0} = \rho \quad \dots \dots \dots (32)$$

(23.3) becomes

$$\begin{aligned} [w^2(r^2 - \tau q^2) - 1 + \zeta^{-1} q^2 U_T^2 - i w r \rho] [(w^2 \zeta r + r - i w \rho \zeta)^2 - W_1^2 w^2 \zeta^2] \\ - (w^2 r^2 + r^2 \zeta^{-1} - i w r \rho) (W_T^2 w^2 \zeta^2 + q^2 U_T^2) \\ - w^2 r \zeta q U_T S_0 = 0, \quad \dots \dots \dots (23.4) \end{aligned}$$

where

$$S_0 = 2W_1 W_T \cos \theta \quad \dots \dots \dots (33)$$

In accordance with the Theory of Relativity we must always have

$$U_1 < c, \quad U_T^2 < c^2 - U_1^2 \quad \dots \dots \dots (34)$$

The equation of condition (23.3) (or its equivalent (23.4)) has at the least three physical aspects, namely :

I. It specifies the possible frequencies and coefficients of damping (or of secular growth) of waves which traverse the medium with a given (real) phase-velocity q^{-1} .

II. It specifies the possible refractive indices and coefficients of attenuation (or of spatial growth) under which waves of a given (real) frequency ω are propagated in the medium, i.e. it specifies the optical dispersion of the medium.

III. It specifies the possible frequencies and coefficients of damping (or of secular growth) of waves which can exist in the medium with a given (real) wavelength λ .

The general discussion of each of these aspects is very complicated ; for example Aspects II and III require, in general, the study of equations of the eighth degree.

Nevertheless it has been found possible to derive from (23.4) a number of interesting physical conclusions when the collision frequency ν is taken to be so small that ρ^2 is negligible.

When that is the case (23.4) reduces to the form

$$f(w, q) \equiv P(w^2, q) + i \rho r w Q(w^2, q) = 0 \quad \dots \dots \dots (23.5)$$

where $P(w^2, q)$ and $Q(w^2, q)$ are certain polynomials.

When the equation

$$P(w^2, q) = 0 \quad \dots \dots \dots (35)$$

is satisfied by a pair of values of w and q which are both real the corresponding wave will be called one of the First Species.

When (35) is satisfied by a pair of values of w and q such that at least one is complex the corresponding wave will be called one of the Second Species.

It has been found that under certain conditions a wave-group, composed of waves of the Second Species with frequencies in a narrow band about the frequency ω , can grow in amplitude as it progresses.*

* When the motion of the positive ions is also taken into account it is found that besides these growing wave-groups we can now find waves of a given length which everywhere *grow with the lapse of time*.

This deduction from the theory suggests one explanation of the origin of stellar, solar and ionospheric noise.

The details of this work and other consequences of the present theory will be published in due course.

APPENDIX.

In the steady state when $d\mathbf{U}/dt=0$ (6) reduces to

$$\mathbf{v}\mathbf{U}-\check{\Omega}_0 \times \mathbf{U}=\mathbf{R} \quad \dots\dots\dots (36)$$

where

$$\mathbf{R}=-\sigma\mathbf{E}_0-N^{-1} \text{grad } \tau N, \quad \dots\dots\dots (37)$$

and $\sigma=-e/m$.

From (36) we obtain

$$\mathbf{U}=\mathbf{P}\mathbf{R} \quad \dots\dots\dots (38)$$

where P is the operator

$$P=(\mathbf{v}^2+\Omega_0^2)^{-1}[\mathbf{v} \dots +(\check{\Omega}_0 \times \dots)+\mathbf{v}^{-1}\check{\Omega}_0(\check{\Omega}_0 \dots)] \quad \dots\dots (39)$$

When $\text{grad } N=0$ and \mathbf{E}_0 and \mathbf{H}_0 are uniform \mathbf{U} becomes the drift velocity \mathbf{U}_0 and (38) then yields

$$\mathbf{U}_0=\mathbf{P}(-\sigma\mathbf{E}_0). \quad \dots\dots\dots (40)$$

From (38) and (40) we obtain

$$N\mathbf{U}=N\mathbf{U}_0-\mathbf{P}\tau \text{grad } N. \quad \dots\dots\dots (41)$$

The last term in (41) represents the diffusion of the electrons. On comparing it with (40) we deduce the following results:

The coefficients of diffusion along and transverse to the magnetic field \mathbf{H}_0 are proportional to the corresponding components of the drift velocity due to an electric force parallel to $\text{grad } N$.

This is equivalent to the results given by Townsend in Sections 91 and 92 of his book "Electricity in Gases" (Clarendon Press, 1915).

Townsend's formulae for the components of \mathbf{U}_0 along and transverse to \mathbf{H}_0 are also easily deduced from (40).

ASPECTS OF THE DIELS-ALDER REACTION.

PART III. A NOTE ON THE REPORTED REACTION WITH ANTHRAQUINONE.

By R. M. GASCOIGNE
and K. G. O'BRIEN.

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There appears to be little doubt that the Diels-Alder reaction does not take place with aromatic rings having a high degree of "aromatic character" except in the special cases where a double bond is conjugated with the ring. The polycyclic aromatic hydrocarbons which undergo the reaction—sometimes with unfavourable equilibria—contain either activated *meso* positions as in anthracene or a relatively fixed and sterically favourable system of double bonds as in perylene. The simple aromatics which react normally are limited to a few highly substituted thiophenes and furan and its derivatives, in which case again the reaction is markedly reversible.

On this view it seemed advisable to investigate a statement by Norton (1942) in a review of the Diels-Alder reaction that a benzene ring of 9, 10-anthraquinone can act as a diene in the reaction and can undergo 1, 4-addition of maleic anhydride. Such a reaction seems unlikely, particularly in view of the similar electron-deficient nature of the benzene rings of anthraquinone and the double bond of maleic anhydride. Norton quotes as authority a paper by Diels and Alder (1929) to which is attributed also an unlikely proof of the structure of the adduct. Perusal of this paper, however, fails to reveal any mention of adduct formation with anthraquinone, and as far as we can discover the subject is not mentioned in any of the works of Diels and Alder. Norton refers also to an observation by Morrell and Samuels (1932), who, in an account of an unrelated investigation, briefly mention that no reaction takes place between maleic anhydride and anthraquinone. These authors make no reference to any previous work on the subject.

In view of the theoretical interest of such a reaction, the following experiments were undertaken in an attempt to isolate an adduct. A range of temperatures was employed since equilibria in adduct formation are considerably affected by temperature. (Bachmann and Kloetzel, 1938.)

- (1) A solution of anthraquinone (2 g.) and maleic anhydride (10 g., molar ratio 10 : 1) in benzene was refluxed for eight hours.
- (2) A solution of anthraquinone (2 g.) and maleic anhydride (10 g.) in nitrobenzene was refluxed for two hours.
- (3) A melt of anthraquinone (2 g.) and maleic anhydride (10 g.) was held at 200 for two hours.

In all cases both the anthraquinone and the maleic anhydride (as maleic acid) were recovered almost quantitatively and no indications of adduct formation could be found. It is concluded, therefore, that anthraquinone does not react with maleic anhydride in the Diels-Alder reaction.

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CONTRIBUTIONS TO THE STUDY OF THE MARULAN BATHOLITH.*

PART I. THE CONTAMINATED GRANODIORITES OF SOUTH MARULAN AND MARULAN CREEK.

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With Plates VIII, IX.

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INTRODUCTION.

The Marulan batholith is a composite intrusion outcropping over a large area which trends more or less northward from the Bungonia-Marulan district towards Wombeyan Caves. It has been the subject of considerable attention at intervals throughout more than forty years (see Woolnough, 1909; Osborne, 1931; Naylor, 1939), but detailed studies upon it are still in progress. Naylor was of the opinion that the intrusion was probably to be assigned to the Late Middle Devonian diastrophism, and when one considers the question of age comparatively in the light of our knowledge of the major Palæozoic tectonic episodes in eastern Australia, there seems little doubt that Naylor's view is correct.

It is clear to the writer that the only satisfactory way to elucidate the geological history and petrological evolution of this batholith is by carrying out detailed petrological investigations upon the relations of the various components, including studies in hybridism and in the contamination by country-rock, which is so widely present throughout the mass.

* The author gratefully acknowledges financial help from the Commonwealth Research Grant in connection with this work.

Various members of the Marulan batholith have been contaminated by the sedimentary rocks through which it has broken. Due to the varied *terrain* invaded by the complex, there is a considerable range of assimilation-effects. The Silurian limestones of South Marulan provide a striking endogenic reaction, and the Ordovician slates and phyllites of the eastern part of Glenrock Estate have also played an interesting part in a series of reactions with the granodiorite. We shall examine these two cases in this paper.

GRANODIORITE CONTAMINATED BY LIMESTONE AT SOUTH MARULAN.

The general relations of these rocks to the associated exogenic zone has been figured and described by the writer in another paper (1931). A brief description of the contaminated granodiorite was given, but more chemical work has now been done on the problem and the present communication supersedes the earlier statement.

Skarns are intimately associated with the altered granodiorite and it is really difficult sometimes to separate the two groups. This is due to the following sequence of processes having operated:

- (a) Crystallization of contaminated magma.
- (b) Limited pneumatolytic activity.
- (c) Hydrothermal action contemporaneous with skarn development.

The last-named processes, while responsible for the metasomatism of calcite, also altered the contaminated rocks, strongly.

These rocks, as a whole, have an igneous aspect, being dark in colour and showing abrupt textural variations. They are cut by aplitic and quartzose strings and veins, and also with prehnite. The last-named occurs as a constituent of some of the rocks, but its presence in veins is due to epigene action.

Unfortunately a complete gradation between granodiorite and modified rock is not traceable, but after the intervention of some soil the contaminated rocks are found about 35 feet from the pure granodiorite. There is no doubt whatever that the latter is the parent or unaltered type. For so large an intrusion as the Marulan batholith the endogenic zone at South Marulan is quite narrow.

Towards the junction of exogenic and endogenic zones the contaminated types become coarser than elsewhere and the dark constituents show idiomorphic character making them conspicuous against the lighter ground of felspar or prehnite. Erratic variations in the proportions make for inhomogeneity, and altogether the lithology is distinctive. The rocks can best be dealt with as follows:

- (a) Contaminated granodiorite, generally hydrothermally altered.
- (b) Pyroxenites.
- (c) Diopside-prehnite rocks.

PETROGRAPHY.

(a) *Normal Granodiorite (Basic Variety).*

This rock is fairly even and medium grained, and presents little of special interest except that it is more basic than the bulk of the Glenrock mass. Nevertheless, it represents the uncontaminated magma of this district. The minerals present are plagioclase, orthoclase, hornblende, biotite, quartz, sphene, apatite, magnetite, zircon and pyrites. The plagioclase is zoned, An_{40} to An_{25} , the central zones being altered to sericite, calcite, kaolin and zoisite. Poorly cleaved and cloudy potash felspar and interstitial quartz are present. The biotite has weathered to chlorite, and notable amounts of secondary sphene, and occasionally sericite, form inter-cleavage masses. Hornblende is weakly pleochroic with X =pale straw-coloured, Y =brownish green and Z =light brown, $Y \gg Z > X$.

The extinction is $\hat{Z}c=14^\circ$. Decomposition to chlorite is fairly prevalent. The fabric is monzonitic, the orthoclase and quartz being completely xenomorphic. There is no pyroxene in the normal rock from this locality. An analysis of the granodiorite is given below.

SiO ₂	57.66		
Al ₂ O ₃	17.36		
Fe ₂ O ₃	6.54		
FeO	0.94		
MgO	4.07	Norm.	
CaO	7.28	Quartz ..	17.28
Na ₂ O	1.56	Orthoclase ..	8.34
K ₂ O	1.38	Albite ..	13.10
H ₂ O	2.24	Anorthite ..	35.31
H ₂ O	0.20	Corundum ..	0.41
CO ₂	abs.	Hypersthene ..	20.36
TiO ₂	0.55	Magnetite ..	1.39
P ₂ O ₅	0.14	Apatite ..	0.40
MnO..	0.04		
			99.96		

Sp. Gr.=2.82

Normative plagioclase, Ab₂₇An₇₃

Granodiorite, South Marulan. Anal. W. H. Hordman.

(b) Contaminated Granodiorite.

The outstanding feature in these rocks is the abundance of well-developed diopside-hedenbergite crystals which are prismatic up to a maximum length of 5 mm. Grey in thin section they show good cleavage and much twinning. The general properties are very close to those of the pyroxene in the rocks of group (c), the chief difference being in a higher diopsidic content, the extinction being $\hat{Z}c=39^\circ$. The other minerals are plagioclase (now much altered), microcline-micropertthite, idiomorphic sphene with occasional ilmenitic nuclei, prehnite, clinozoisite and apatite. Frequently the only indication of plagioclase are the outlines of pseudomorphs, but in a few places its composition is determinable at approximately an average of An₅₆. The decomposition of plagioclase has yielded scapolite, calcite, zoisite, sericite and kaolin, some of these being due to pneumatolytic and hydrothermal action. Potash felspar locally increases in some rocks where quartz is also developed, and these are clearly due to infiltration and related to the pegmatitic material veining the contact. Clinozoisite has characteristic interference colours and strong cleavage. The sphene is noticeably pleochroic with the following scheme: X=pale yellow, Y=pale greenish yellow, Z=reddish brown, $Z \gg Y > X$. Interference figures bespeak a small optic axial angle. The prehnite in these rocks is deuteritic in origin; it shows general turbidity and the typical features of aggregate extinction, etc., so common in this mineral.

(c) Pyroxenite.

Some parts of the contaminated mass are composed almost entirely of diopside-hedenbergite so that the rock may be termed pyroxenite. The specimens pass eventually without sharp junctions into the other types. Although not abundant, these rocks may be obtained in specimens up to one foot in

diameter. The pyroxene is a little more ferriferous than that in the previous groups of rocks, and its optical properties and composition are shown hereunder.

	(3)	(1)	(2)	Metal Atoms on Basis of 6 (O).	
SiO ₂ ..	50.91	49.48	50.28	1.962	1.99
Al ₂ O ₃ ..	0.17	1.17	1.19	.028	
Fe ₂ O ₃ ..	.76	.14	.15	.002	
FeO ..	17.34	16.52	16.80	.545	1.019
MgO ..	7.21	7.13	7.25	.423	
MnO ..	.21	.60	.60	.018	
TiO ₂ ..	—	.40	.41	.011	.973
CaO ..	22.93	23.59	23.32	.973	
P ₂ O ₅ ..	—	.64	—	—	
H ₂ O ..	—	.10	—	—	
	99.53	99.77	100.00	(Ca, Mg, Fe'', Fe''', Mn, Ti) ₂ (Si, Al) ₂ O ₆	

2V (+) Medium

$\hat{Z}c = 47^\circ$

$\alpha = 1.698$

$\beta = 1.705$

$\gamma = 1.720$

$\gamma - \alpha = 0.022$

Fe/Mg = 3.02

1. Diopside-hedenbergite from pyroxenite, Sth. Marulan. Anal. Naima Sahlbom.
2. The same, after deducting apatite and water.
3. Pyroxene, Nordmark, Sweden. (Iddings Rock Minerals, p. 300.)

The analysis shows the mineral to be a normal member of the diopside-hedenbergite series with molecular constitution such that He/Di = 58.39. The mineral has little titanium which belongs to the Y group entirely.

The similarity of the Marulan and the Swedish minerals is very noticeable, and it is to be remarked that they occur with somewhat similar parageneses.

On the other hand the pyroxene from pyroxenite in the endogenous contact at Scawt Hill (Tilley, 1929) is more diopsidic, the ratio Fe/Mg being 0.71.

The Marulan pyroxene is low in alumina and thus is in contrast with the type of aluminous pyroxene which Tilley (1938) has shown to be characteristic of some limestone contacts. In some of these cases at least the associations are different from that of Marulan in that the pyroxenes come from exogenic contacts and have not been precipitated from magma.

The accessories in the pyroxenic rocks which rarely aggregate more than 3% are sphene, apatite and a little turbid felspar.

(d) *Diopside-prehnite Rocks.*

These occur with either of the foregoing in the most irregular fashion. They consist of diopside-hedenbergite and prehnite with a few accessories comprising apatite, sphene, a little potash felspar and some introduced quartz.

The prehnite, which is primary, occurs in well cleaved plates and sheaf-like masses, these being for the most part quite clear. Contiguous with such material there is a good deal of very turbid prehnite, and the two varieties grade into one another. The mineral shows shadowy extinction, good cleavage, and has a noticeably small (+) 2V, while the sign of the elongation varies.

The diopside, which is identical with that in rocks of group (b), may be so well developed as to cause the prehnite to be relegated to an intergranular position, or alternatively the small idiomorphs of pyroxene may lie embedded, poikilolitically, in large masses of prehnite. A certain amount of excess calcite is often seen.

Chemical Discussion.

The contaminated rocks are the result of precipitation from a modified magma; they are not related to the pure granodiorite in the sense that reaction made over such a rock into a contaminated product. There is no sign, for example, of "regenerative crystallization" in the sense put forward by Kennedy and Read (1936). Lime-enriched liquid, which was being depleted in other constituents, began to crystallize as pyroxenite, and later continued on with the formation of the other types already described.

The study of the pyroxenes indicates that the variety in the pyroxenites is more feriferous than any in the surrounding rocks. Although no analysis of the contaminated rock is available, the knowledge of the general modal percentages (by volume) allows us to conclude that in a contaminated type with 45-50% of diopside the proportion of FeO in the rock would be approximately equal to the percentage in the pure granodiorite (see above).

The composition of the pyroxenite must be almost the same as that of the pyroxene. As stated, the Fe/Mg ratio in the latter is 3.02, while in the pure granodiorite it is 2.17. Thus the pyroxenite is partly due to a local concentration of iron at the expense of MgO. This has led to an enrichment of the neighbouring magma in MgO at least, and possibly in other oxides. Some of the magnesia freed by the increase of the hedenbergite molecule in the pyroxene has been fixed in diopside in the lime-silicate rocks, and the rest has helped to build the slightly more diopsidic pyroxene of the contaminated granodiorite. While the crystallization of the pyroxenite and granodiorite was in progress some constituents were migrating to the exogenic zone. Earlier study of that zone has shown that considerable amounts of silica and alumina, some magnesia and small quantities of iron and potash left the magma for the limestone. Nothing but lime was received in return, which was instrumental in effecting a conversion of the hypersthene molecules of the granodiorite (see norm) into diopside-hedenbergite molecules.

Now if we eliminate the infiltrated quartz and orthoclase from these rocks and ignore the pneumatolytic and deuteric action, we see that the granodiorite magma with the abovementioned oxides removed, would approximate to a liquid which would produce by crystallization a monzonite or diorite-gabbro. The addition of lime has been to modify such a magma to a composition which would determine the separation of abundant diopside-hedenbergite, as the first of a new reaction series. The continual supply of lime led to the combination of the whole of the (Mg, Fe)O available, and further promoted the growth of idiomorphic sphene, the TiO_2 of the magma being shared between this mineral and the diopside. After most of these minerals had developed the aluminosilicates separated, the plagioclase preceding the micropertthite. The lime-soda feldspar was not labradorite and the slightly perthitic potash-feldspar received its soda according to one of two sets of conditions; either (a) the basification and diminution in volume of the plagioclase led to a little surplus Na_2O , or (b) in the gradual depletion of the magma in alumina (due to its migration to the limestone) that which was left united with potash because of strong affinity with this alkali, and thus labradorite could not continue to form, and any soda left was taken up in perthite. A corollary, under normal conditions, of this would be zoning of the plagioclase to give a more acid periphery, but this was prevented by the onset of pneumatolytic and deuteric activities which allowed the water of the magma to become effective, and prehnite and other hydrous aluminosilicates were formed. Scapolite and sericite were also produced in some quantity and a good deal of kaolin developed. Some structural changes, chiefly in the nature of shrinkage-effects, made possible the invasion of salic liquid, and this is expressed in the acid veins and strings to be seen through all rocks.

Such is the probable evolution of the contaminated rocks of groups (b) and (c). It only remains to explain that the primary prehnite of the diopside-prehnite rocks took the place of labradorite when circumstances were such that insufficient alumina was available for practically any feldspar to form, and (OH) was active.

We see, then, that a profound change in the molecular constitution took place in the altered granodiorite magma and the trend of crystallization was radically altered from the normal granodiorite sequence, chiefly due to the following factors :

- (a) Subtraction of SiO_2 , Al_2O_3 , MgO and K_2O .
- (b) Addition of lime.
- (c) Concentration of iron in a lime-enriched magma resulting in pyroxenite crystallizing.
- (d) Onset of pneumatolysis and later hydrothermal activity in which water played a leading part.

The relations of the combinations of the oxides in the unaltered and contaminated rocks is shown in a summarized form on page 122.

GRANODIORITE CONTAMINATED WITH SHALE-CALCIC HORNFELS, ETC.

Field Occurrence.

The greater part of Glenrock Estate, south-east of Marulan, is given over to granodiorite now exposed on the plateau surface and in the gorge of Barber's Creek and the tributary stream beds, which are mostly on the tableland. An examination of the granodiorite throughout the Glenrock area leads one to conclude that a considerable portion of the rock is contaminated by sedimentary material and also that the last episode in the crystallization history of the mass has been a fairly strong deuteritic activity. The presence of rhombic and monoclinic pyroxenes in the granodiorite was recorded by Woolnough. It is significant that in the areas where the granodiorite is pyroxene-free there is an absence of evidence of contamination, such as inhomogeneity, "strew" from digested xenoliths, and in general a minimum of hydrothermal products. In particular the mineral epidote, which is abundant in the deuterically altered phases and in the aplites and pegmatites, is rarely seen. Again, any xenoliths present show very little reaction. All these features suggest that more advanced contamination was made possible because of conditions of relatively low temperature and abundance of volatiles just at the close of the pneumatolytic stage. These conditions obtained at least on the eastern margin of the complex.

The prevalence of contamination effects in the rocks of Glenrock Paddock and the great abundance of inclusions with reaction rings along the eastern side of the complex confirms the suggestion of Woolnough (1909, p. 786) that the present ground-surface is not greatly removed from the former rather flat upper surface of the batholith.

It is not within the province of this paper to deal with the petrogenetic problems of the granodiorite, but to consider the reaction between it and several types of hornfelses which occur as xenoliths.

In Marulan Creek near where it begins to descend through a tributary gorge to Barber's Creek there are excellent exposures of the contaminated and xenolithic mass. Here one is near the margin of the batholith where the fragments of country rocks are very abundant. The granodiorite forming the host to these is variable in texture, and is seamed with streaky as well as sharply bounded veins of aplitic and pegmatitic material. In these orthoclase reaches a large pro-

portion of the whole, and epidote is common. The latter has been the last mineral to crystallize, filling druses in the central parts of the veins. Beautiful dark green crystals are frequently to be seen.

The inclusions are of all sizes up to about one foot in diameter, and show more or less rounded outlines in the majority of cases. Sometimes where injection of magma has taken place along bedding planes there has been early disintegration before reaction and angular fragments often persist. At other times perfectly rounded contours give rise to spheroids.

In almost every case the xenoliths are surrounded by well-defined reaction rings which vary greatly in thickness. This variation appears to be related to the size of the fragment and the availability of volatiles for the reaction process. The appearance of the inclusions with their coronæ of more salic minerals is very characteristic. The rings have a predominantly pink colour due to the abundance of feldspar which has weathered more readily than that in the parent rock.

Examining the reaction rings more closely one sees that almost invariably there are three zones between the main portion of the inclusion and the relatively unaltered granodiorite. Succeeding the main mass of the inclusion, near its margin there is the following sequence:

- (a) A narrow zone of greenish-grey material of very fine grain size.
- (b) A still more restricted zone of speckled material in which hornblende is discernible.
- (c) A medium-grained igneous zone consisting of abundant feldspar and quartz with some hornblende or chlorite.

In some inclusions the zone (b) is not easily distinguished, but it is generally apparent under the microscope. A photograph (see Plate VII, fig. 4) shows a typical inclusion with reaction ring. A certain amount of injection of the marginal zone of the inclusion is also shown.

The width of the reaction areas may be as much as three inches in xenoliths of about eight inches diameter.

The weathering of the xenolithic granodiorite varies for some reason not yet apparent. Generally the surface of parent rock and xenolith is uniformly eroded, but in places (e.g. in Marulan Creek near Portion No. 19) the xenoliths have been responsible for a nodular structure which gives the rock the appearance, in the distance, of a differentially weathered conglomerate. In this type it is necessary to break open the resistant reaction material of the spheroids before the nature of the xenolithic nucleus can be examined.

PETROGRAPHY.

(1) *The Least Modified Granodiorite.*

In view of the uncertainty as to whether any of the granodiorite in the neighbourhood of the inclusion zone is uncontaminated, we shall employ the adjective "least-modified" here for the material definitely distinct from the endogenic reaction rings.

W. G. Woolnough gave a good account of the granodiorite from Glenrock Falls (which are near the area of contamination), and recorded the presence of both diopside and hypersthene. The analysis from Woolnough's paper shows distinct differences from the analysis (given above) of a somewhat basic phase of the granodiorite. This basic phase is regarded here as the equivalent of the unaltered rock of the Glenrock Estate. The former analysis appears to bear a similar relation to the latter as does an analysis (given below) of the modified granodiorite of Marulan Creek.

Almost all the slices of granodiorite examined show much evidence of hydrothermal alteration. This, it is believed, followed the reaction which took place between magma and hornfels.

The minerals seen under the microscope are *plagioclase*, *potash feldspar*, *amphibole*, *biotite*, *quartz*, *magnetite*, *apatite*, *zircon*, and a good deal of *chlorite* of varying colour, and significant *epidote*.

The *plagioclase*, which is strongly zoned, is difficult to determine, but the average composition is from An_{50} to An_{25} for the main part of the crystal, while the outermost zones are of clear andesine-oligoclase. The alteration products are kaolin, epidote, scapolite and calcite.

The *potash feldspar* is slightly perthitic at times, but otherwise appears to be orthoclase, and is always heavily kaolinized. The *amphiboles* are in confused groups of subidiomorphs showing remnants of twinning. There are at least two varieties. One is pale green to grey and has $Z\hat{c}=14^\circ$, while the other is finely fibrous and of darker green colour, and shows the properties of uralite. The whole of the aggregates show patchy coloration and extinction, and there are evidences of volume changes consequent upon hydrothermal action. The pale variety is sometimes close to tremolite in composition. Its R.I. is $\beta=1.661$.

Biotite is reddish-brown with epidote, sericite and sphene as alteration products along the cleavage, while extensive change to chlorite is seen throughout most of the flakes. In fact chlorite is one of the most characteristic constituents of all the rocks in the eastern side of the Marulan complex. The deposition of epidote and sericite in the cleavages with bending of the cleavage planes due to volume changes is distinctive, and forms a useful feature when comparison of modified hornfels and granodiorite is investigated. The biotite has $\beta=1.643$.

Quartz is interstitial and shows fluid inclusions. The fabric of the rock is subidiomorphic granular to sub-monzonitic.

(2) *The Xenoliths.*

There is not a great variety amongst the inclusions. They are clearly the thermally metamorphosed equivalents of Ordovician slate and quartzite, and occasionally of calcareous shaly material.

Some interesting study is to be had from the standpoint of the thermal metamorphism of these types, but that will not be dealt with here. It is sufficient to point out that under the conditions of sudden elevation of temperature and relatively quick cooling, the small fragments immersed in a magmatic medium have recrystallized, sometimes giving unstable assemblages in which extra phases are present above the number expected under equilibrium conditions. The types examined in order of abundance are :

- (a) Andalusite-cordierite-spinel-plagioclase hornfelses.
- (b) Sandstone hornfelses.
- (c) Cordierite-hypersthene-plagioclase-spinel hornfelses.
- (d) Hypersthene-diopside-plagioclase hornfelses.

(a) *Andalusite-cordierite-spinel-plagioclase Hornfelses.* In these rocks sillimanite may occur in fair abundance along with the other minerals. In all rocks orthoclase is an important constituent. Biotite is absent from the central parts of xenoliths and develops near to the reaction border. Until further work is done upon the group of hornfelses as a whole it is not possible to decide whether some of the biotite-bearing rocks owe their mica purely to thermal change or to the effects of magmatic reaction. In this section the rocks which clearly show biotite as a product of reaction are considered.

The rocks are very fine grained and have a resinous lustre. The minerals present are cordierite, orthoclase, plagioclase, andalusite, pleonaste, magnetite, zircon and perovskite. *Cordierite* is abundant in twinned and ragged units, which are strongly sericitized or pinitized. Haloes around zircon are very well

developed. *Andalusite* is xenoblastic, and has many inclusions. The *spinel* is very subordinate and is associated with magnetite. The *plagioclase* is andesine, and is never abundant. *Orthoclase*, on the other hand, is prolifically developed.

As the magmatic contact is approached the cordierite shows more alteration, sometimes to a yellow isotropic mass, and eventually fails, and biotite begins to make its appearance. It is generally found intimately connected with iron ore and spinel. It has the same general colour and refraction of the biotite of the granodiorite, and also shows in places the peculiar intercleavage masses of epidote or sericite which are found in the igneous rock.

In the greyish-green zone the potash felspar is now strongly kaolinized and plagioclase has become acidified so as to be almost pure albite, although it is also decomposed. The iron ore decreases and andalusite disappears. A considerable amount of granular epidote is found through the turbid zone.

The stages of development of biotite from cordierite and iron ore, involving also probably the using up of the small amount of spinel present, can be seen in the inner border of the turbid zone. Partly chloritized cordierite merges into olive-green biotite which, with incorporation of more iron, becomes brownish and eventually is similar to the mica in the granodiorite. In some of the modified hornfelses the plagioclase is a little more basic than in the unaltered rock. Whether this is due to an original higher calcic character or not is difficult to determine.

At this stage the reciprocal changes were "arrested" by congealing of the magma and further development was in the nature of a deuteric hydration.

In the granodiorite the change in the neighbourhood of the inclusions is easily perceived and needs little description. A slight concentration of quartz and felspar and a decrease of ferric material are the chief features. The felspar is partly plagioclase, but mostly orthoclase. The magma therefore is definitely depleted in ferromagnesian content and receives additional potash. Some analyses dealing with this reaction are given in Table 1.

(b) *Sandstone Hornfelses*. The prevalence of quartzites in the Ordovician rocks of the district leads to the relative abundance of gritty and quartzitic hornfelses in the xenoliths. The central parts of such inclusions show grains of quartz and a little alkali-felspar cemented by chloritic material which, under high magnification, appears to have been partly recrystallized into biotite and cordierite which has iron ore inclusions. The quartz and felspar may have recrystallized, but this is not absolutely clear. The effect of the immersion in magma has been to increase the biotite content due partly to addition of potash and partly to crystallization of detrital material. The change in the magma appears to be practically nil.

(c) *Cordierite-spinel-hypersthene-plagioclase Hornfelses*. These have fairly coarse grainsize, the cordierite and plagioclase reaching a maximum of 3 mm. diameter. The former is not altered greatly and shows strong chequer-twinning. The plagioclase is labradorite (about An_{52}) with finely drawn albite twinning. Hypersthene is rather striking with pleochroism, X=wine coloured, Y=greyish yellow, and Z=greyish green, and is in extremely irregular grains suggesting low crystalloblastic position.

These hornfelses are only slightly deficient in silica for the spinel is very subordinate, occurring as dark blebs and strings through plagioclase. There is no orthoclase in the typical rock, and no thermal biotite.

The changes in this type of xenolith as the granodiorite is approached are very interesting. Hypersthene, with its iron-ore clots, begins to change to a pale pyroxene, then to green hornblende and eventually to olive green biotite. The last-named sometimes develops directly at the expense of the iron ore and

pyroxene. In this case potash must come from the magma, as it is not available in the hornfelses. The cordierite, unlike that in rocks of group (a), does not go over to biotite so readily, due perhaps to the role being played by hypersthene and to the dearth of potash. It appears to change to sericite and then to disappear when green hornblende develops along the periphery of the inclusions. This hornblende is idiomorphic, shows a greenish blue colour, and has the extinction angle of an actinolitic variety, $\hat{Z}c=18^\circ$. Spinel disappears on the addition of quartz or at the growth of biotite, and the plagioclase is acidified in this case—a feature somewhat contrasting with the plagioclase in rocks of group (a). There is less orthoclase in this turbid zone and the rather abrupt succession of

- (i) Cordierite-spinel-hypersthene-plagioclase,
- (ii) Plagioclase-cordierite-biotite
- (iii) Plagioclase-quartz-orthoclase-hornblende

shows clearly the state of inequilibrium when the reactive processes were arrested.

In the magma, as a result of a concentration of hornblende at the margin of the inclusion, there is a general increase in salic constituents. Deuteric activity has caused the change from hypersthene to bastite. No analysis for these reactions is available.

(d) *Hypersthene-plagioclase-diopside Hornfelses.* These belong to a more calcic type, of which a few representatives are seen. They have a little orthoclase but no original biotite. As indicated below, all the biotite is due to reaction. *Diopside* is almost colourless, occurring in stout prisms set in *plagioclase* which is poorly twinned and slightly zoned and has a composition of basic andesine to acid labradorite. The *hypersthene* is present in rounded grains arranged in groups and strings. It is dark brown and shows fairly strong pleochroism, and is associated with iron ore.

The effect of the magmatic environment has caused a very decided change in the rhombic pyroxene, but not in the diopside. The former passes to a pale diopsidic type and then to leek-green hornblende and finally to olive-green biotite. The diopside remains right up to the border zone and then only sluggishly reacts to give some biotite if iron ore is available. Orthoclase is now wanting and there is a good deal of more acid plagioclase. The effect of the later deuteric solutions has been to give much epidote and some kaolin in the peripheral zone of the xenoliths.

The magma has experienced much the same modification as detailed in the last subsection. A migration of potash and quartz has led to enrichment in quartz-feldspathic constituents at the junction.

Chemical Discussion.

In Table 1 are given analyses of (1) a cordierite-andalusite-spinel-plagioclase xenolith, (2) an altered xenolith which had developed a certain amount of biotite and hornblende, (4) modified granodiorite from the neighbourhood of the inclusions, and (5) a basic phase of the granodiorite (already discussed in last section).

In regard to the comparison of (1) and (2), it is to be remarked that on account of the uniformity of texture and general constitution of the hornfelses of type No. (1) the selection of a rock which has been in the general condition of (2) is justified. Each rock having been solid at the time of immersion in magma, it is possible to compare volumes, based on densities. This has been done (see Table 1).

It will be seen that the most important changes are as follows :

The xenolith has given alumina, titanium and potash to the magma, and has gained significant CaO, MgO, iron and Na₂O.

The actual amounts shown in Table 1 must not be taken into account so much as the qualitative effect of the changes, as indicated by the chemistry and petrography of the study. Thus when viewing the changes in the magma by inspection of (4) and (5) we note that the concentration of alkali feldspar around the inclusion is indicated in the higher values, in (4), for silica and alkalis, the alumina having been more than sufficient to satisfy the increases of Na_2O and K_2O . On the other hand there is a distinct decrease in MgO , FeO and CaO , and this is correlated with the changes in the xenolith.

TABLE 1.

	(1)	(2)	(3)	(4)	(5)
SiO_2 ..	51.68	51.37	51.92	61.96	57.66
Al_2O_3 ..	25.86	22.96	23.21	15.82	17.36
Fe_2O_3 ..	0.48	1.70	1.72	1.56	0.94
FeO ..	6.63	5.92	6.01	4.60	6.54
MgO ..	3.29	4.31	4.36	3.26	4.07
CaO ..	0.61	2.02	2.04	4.84	7.28
Na_2O ..	2.82	3.38	3.41	2.17	1.56
K_2O ..	5.18	4.77	4.82	2.48	1.38
H_2O ..	2.28	2.65	2.68	2.25	2.24
H_2O —	0.10	0.10	0.10	0.16	0.20
TiO_2 ..	0.72	0.59	0.60	0.52	0.55
MnO ..	tr.	tr.	tr.	0.05	0.04
P_2O_5 ..	0.06	0.12	0.12	0.15	0.14
CO_2 ..	0.12	abs.	---	abs.	abs.
	99.83	99.89	100.99	99.82	99.96
Sp. Gr. ..	2.72	2.75	2.75	2.76	2.82

Normative plagioclase, $\text{Ab}_{43}\text{An}_{57}$ $\text{Ab}_{27}\text{An}_{73}$.

	plagioclase	Norms.	
		(4)	(5)
1. Andalusite-cordierite-spinel xenolith. Marulan Creek.		Quartz 21.12	17.28
		Orthoclase 15.01	8.34
2. Modified inclusion, Marulan Creek.		Albite 18.34	13.10
		Anorthite 23.35	35.31
3. No. 2 recalculated for comparison with No. 1.		Corundum 0.92	0.41
		Hypersthene 14.44	20.36
4. Modified granodiorite near hornfels xenoliths. Marulan Creek.		Magnetite 2.32	1.39
		Ilmenite 0.34	1.06
5. Granodiorite (basic phase). Sth. Marulan.		Apatite 0.91	0.40
Anal. for all rocks, W. H. Herdsman.			

Here we must be careful to allow for deuteric phenomena in so far as we can determine its mineralogical effects. It appears from microscopic study that the hydrothermal alteration was essentially a hydration, plus a certain amount of albitization, and thus we cannot be sure how much of the excess soda (if any at all) is due to reciprocal reaction before deuteric change. In view of the general principles of contamination it appears likely that the increase of soda, in the xenolith, is apparent and not real. The problem of the interrelation of the deuteric and reactive modifications in magma and inclusion enhances the interest of the present study.

Mineralogical Changes.

Mineralogically we see that the chief rearrangements have been as follows :

- Cordierite, spinel, iron ore and orthoclase have reacted with water and possibly MgO from the magma to give biotite. Sufficient potash in the inclusion (originally 5.18%) allowed enrichment of magma in orthoclase.
- Hypersthene and diopside have given rise to biotite either direct, or through hornblende, the other reacting components coming from the magma, particularly lime and water.

- (c) The part played by the plagioclases is not clear. The acidification which went on in the turbid zone and the concentration of alkali-felspar in marginal magma-zone are partly due to deuteric solutions. It is probable that if the plagioclase of the inclusion were about the same composition as that of the granodiorite, any activity by CaO would be directed to building hornblende.
- (d) The hornblende in the outermost zone of the inclusions indicates the "convergence" which has marked the processes. The goal for the inclusions is determined by the constituents of the granodiorite. It is significant that only one portion of the "convergence field" was reached by the components of the inclusions, that is the range of the ferro-magnesian constituents. Later action would have been in the direction of producing convergence in the matter of the felspar series.

It is seen, therefore, that a rather unbalanced set of transfers operated, but this really emphasizes one of the main advantages of the present occurrence, viz. that the conditions indicated by the assemblages were of a preliminary character when equilibrium had not been established. Thus these rocks give us information about some of the intermediate steps leading to the establishment of reciprocal changes in which definite associations of components are wrought.

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EXPLANATION OF PLATES.

PLATE VIII.

Fig. 1.—Granodiorite (somewhat basic phase) from South Marulan near contaminated zone. Altered plagioclase crystals, subordinate orthoclase, quartz and considerable ferro-magnesian content. Hornblende is subidiomorphic, and biotite shows inter-cleavage mass of epidote. Ordinary light $\times 18$.

Fig. 2.—Diopside-prehnite-orthoclase rock, due to contamination of granodiorite, South Marulan. Crystals of pyroxene associated with intensely kaolinized orthoclase and shapeless masses of prehnite which is deuteric in origin. Ordinary light $\times 18$.

Fig. 3.—Diopside-prehnite rock, South Marulan. Crystals of diopside-hedenbergite are set within masses of prehnite. Note characteristic variable turbidity of the latter mineral. Ordinary light $\times 18$.

Fig. 4.—Pyroxenite from South Marulan. The rock is composed almost entirely of diopside-hedenbergite in well-formed crystals, the accessories being sphene, ilmenite and prehnite. (Rock due to contamination.) Ordinary light $\times 18$.

PLATE IX.

Fig. 1.—Modified granodiorite from Marulan Creek. Concentration of Q, Hb and Or near reaction zone is indicated. Ordinary light $\times 18$.

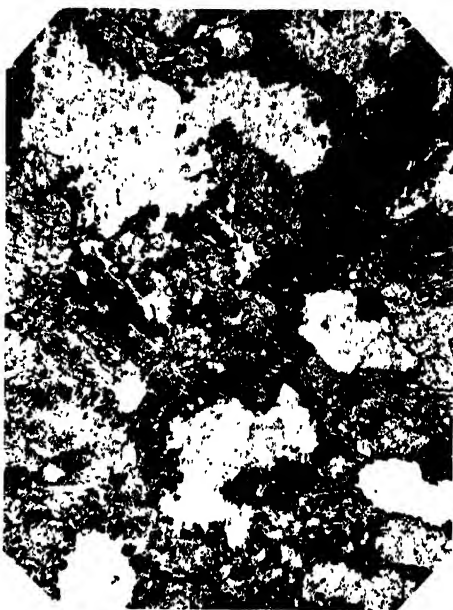
Fig. 2.—Diopside-hypersthene-plagioclase. Abundant dark Hy, paler Di and larger P. Loc., Marulan Creek. Ordinary light $\times 18$.

Fig. 3.—Modified cordierite-hypersthene-plagioclase-spinel rock. Pronounced development of biotite. Xenolith at Marulan Creek. Ordinary light $\times 18$.

Fig. 4.—Hornfels xenolith in granodiorite. Reaction is well shown, also initial marginal disintegration. Three-quarters natural size.



1



2



3



4



1



3



2



4

NITROGEN IN OIL SHALE AND SHALE OIL.

V. THE DETERMINATION OF NITROGEN IN SHALE OIL AND OIL SHALE.

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INTRODUCTION.

The application of the Kjeldahl method for the determination of the nitrogen content of crude petroleum and crude shale oil has been attended by difficulties which appear to have been due mainly to the failure to appreciate fully the various factors involved. For example, when determining the nitrogen content of crude shale oil, Petrie (1) found that twenty days' digestion with sulphuric acid were necessary before the mixture cleared. Since that time, however, catalysts have been used together with added sodium or potassium sulphate in order to speed up the digestion.

The U.O.P. method for the determination of nitrogen in petroleum (2) recommends the continuation of the digestion for from one-half to five hours after the acid clears, but gives neither a reason of the extended time nor any indication of its importance. This method is a simple adaptation of the first successful application of the Kjeldahl method for the determination of nitrogen in petroleum by Poth *et al.* (3). These workers used a mercuric oxide-copper sulphate catalyst with potassium sulphate to raise the temperature of the digestion mixture, and they found that, in order to recover all the nitrogen present, it was necessary to continue the digestion for five hours after the acid had cleared.

SHALE OIL.

This method was modified slightly by reducing the scale of the analysis, and then used as a basis for the determination of the optimum conditions. All aspects of the method were checked in order to render its application as accurate and as simple as possible.

DIGESTION.

With the shale oil it was found most convenient to use approximately two grammes of the sample, as the use of a larger sample gave difficulty with foaming during the digestion, while a smaller sample gave insufficient ammonia on the final distillation. The addition of some paraffin to the digestion mixture, as recommended by U.O.P. to reduce foaming, was found to be quite ineffective.

Samples of crude shale oil were digested for varying times in order to determine the optimum digestion time. It was observed that the time required for the digestion mixture to clarify was not significant, the significant time being that for the subsequent digestion. This result is at variance with Crossley's observation (4) that maximum nitrogen figures were obtained with the minimum heating rate to give the minimum "clearing" time. Subsequent work has, however, indicated that excessive "clearing" times can give low results, but not if the heating is carried out as described in the final method. The results of these tests (Table 1) show that a minimum digestion time of $1\frac{1}{2}$ hours after clarification is necessary. A digestion time of two hours after clarification of the acid was therefore taken as standard.

It is possible that the very slightly lower value obtained after three hours' digestion was due to the volatilization of part of the ammonium sulphate. This explanation was suggested by the observation that if much sulphuric acid was allowed to distill from a sample during the digestion a low, and sometimes negligible, result was obtained. Beet and Furzey (5) also observed that prolonging the digestion much beyond the minimum time required for complete conversion of the nitrogenous material to ammonia was liable to give slightly low results.

TABLE 1.
Effect of Digestion Time on Result.

Digestion Time After Clearing.					Observed Nitrogen Content Percentage.
0 hour	0.393
$\frac{1}{2}$ hour	0.455
1 hour	0.486
$1\frac{1}{2}$ hours	0.520
2 hours	0.521
3 hours	0.514

All results are the average of at least duplicate analyses.

Low results were also obtained if no addition of sodium or potassium sulphate were made to increase the boiling point of the digestion mixture. The time required for the mixture to clarify was increased from between $\frac{3}{4}$ and $1\frac{1}{4}$ hours to between 2 and 3 hours and subsequent digestion times of up to 4 hours continued to give low results (see Table 2).

TABLE 2.
Effect of Digestion with Sulphuric Acid Only.

Digestion Time After Clearing.					Observed Nitrogen Content Percentage.
2 hours	0.347
$2\frac{1}{2}$ hours	0.404
4 hours	0.464

All results are the average of duplicate analyses.

Shirley and Becker (6) observed that, for the determination of nitrogen in pyridine type compounds, copper sulphate was an inefficient catalyst, while mercury was satisfactory.

The catalyst used by Poth *et al.* (3) was a mixture of copper sulphate and mercuric oxide, so their individual efficiencies for the determination of nitrogen in shale oil were examined.

Analyses were run in duplicate using 0.5 gm. of the individual catalysts instead of 0.5 gm. of each with a final digestion time of two hours.

The results were :

Copper sulphate	0.508, 0.520	0.514% N.
Mercuric oxide	0.528, 0.519	0.523% N.
Mixed catalyst		0.520% N.

The differences between these duplicates were greater than customary with the mixed catalyst but were not considered significant. On the basis of this experiment, however, the use of the mixed catalyst was continued.

DISTILLATION.

In order to reduce the amount of attention required during the distillation of the ammonia several minor modifications to the customary set-up were made.

Instead of distilling through a splash trap to retain caustic spray, the ammonia-laden steam was bubbled through boiling water. A Claissen flash was substituted for the simple distillation flask recommended for this purpose by Thorpe and Whitely (7) as being more efficient.

Fitting the distillation receiver with a bunsen valve, as recommended by Meneghini (8) greatly reduced the danger of accidental "suck-backs".

All water used for washing and dilution purposes was carefully redistilled from caustic soda and the first fractions which contained any traces of ammonia discarded. In order to reduce the possibility of contamination the ammonia-free water was stored in glass stoppered bottles and only a minimum stock kept in hand.

Absorption of the ammonia vapours in boric acid solution followed by titration of the ammonia with sulphuric acid using screened methyl red indicator gave more uniform results than absorption in sulphuric acid, followed by back titration with caustic soda solution (Table 3).

TABLE 3.
Difference between Duplicate Analyses.

Acid Used.	Difference between Duplicate Analyses.		Number of Duplicates
	Mean.	Standard.	
Boric	0.0055% N.	0.0068% N.	60
Sulphuric	0.0132% N.	0.0193% N.	25

FINAL METHOD.

The method finally adopted is as follows: The following materials were weighed into a 500 ml. Kjeldahl digestion flask:

40 ± 0.5 gms. sodium bisulphate.

or

30 ± 0.5 gms. anhydrous sodium sulphate.

0.5 ± 0.05 gms. copper sulphate.

0.5 ± 0.05 gms. mercuric oxide.

Approximately two grammes of the crude oil were carefully weighed (to the nearest milligramme) into the digestion flask by means of a Lunge pipette. Forty ml. of concentrated sulphuric acid were added, if sodium bisulphate was used, and 50 ml. if sodium sulphate was used, and the flask rotated to mix the contents. Heating was then commenced with a small flame.

During the first part of the digestion the heating had to be carefully controlled because of the foaming tendencies of the digestion mixture. After the foaming ceased the flask was heated strongly so that sulphuric acid vapours refluxed in the bottom of the neck of the flask but did not distill off. The time at which the mixture turned clear green was noted and the digestion continued for a further two hours. After cooling till crystallization had just commenced the acid was carefully diluted with 100–120 mls. of ammonia-free distilled water. This was done carefully and with shaking to avoid layering in the flask.

This diluted acid was poured into the distilling flask and the digestion flask rinsed with a further 200 ml. of water, which were also added. Two to three grammes of granulated tin or zinc were added with two to three grammes of pure paraffin wax to reduce foaming.

One hundred millilitres of ammonia-free water were charged into the Claissen flask and 50 ml. of 4% boric acid charged into the titration flask and the apparatus connected up (Fig. 2).

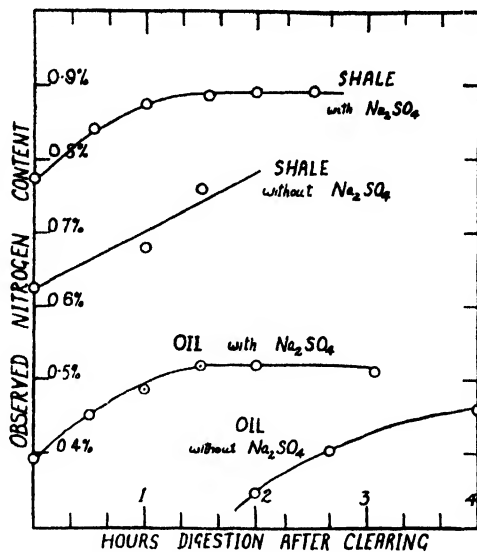


Fig. 1—Effect of Digestion Conditions on the Observed Nitrogen Content of Oil Shale & Shale Oil.

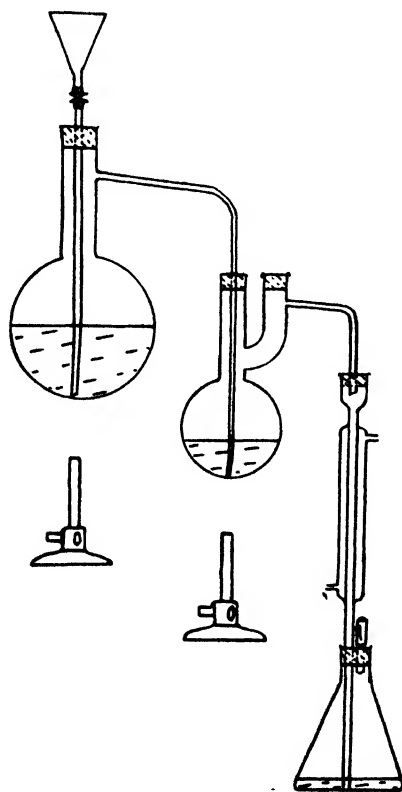


Fig. 2—Distillation Apparatus.

Ten millilitres of 25% sodium sulphite solution (to decompose mercury ammine complexes) were added to 250 mls. of 40% caustic soda solution and the mixture charged to the distillation flask through the funnel. Use of an ordinary glass funnel connected to the delivery tube by means of a length of rubber tubing which could be sealed with a screw slip was quite satisfactory and eliminated the possibility of frozen stop-cocks. After the addition of the caustic soda solution a few bubbles of air were blown through the solution to mix it. Failure to mix the acid and the caustic solution thoroughly could cause serious bumping or even priming when the distillation was started.

The distillation was commenced and the water in the Claissen flask boiled at such a rate that its volume did not change significantly during the process. When approximately 250 mls. of water had distilled into the titration flask the distillation was stopped and the condenser rinsed into the flask with approximately 20 c.c. of previously neutralized water. Four drops of the screened methyl red indicator were added and the solution titrated with decinormal sulphuric acid.

Blank determinations were carried out with a 2 g. sample of sugar or naphthalene on each lot of reagents and at frequent intervals during the process of a long series of analyses.

OIL SHALE.

After the successful application of the Kjeldahl method to shale oil the work was repeated with oil shale to see if the same or different conditions were required. It was found that the digestion proceeded more smoothly with the shale than with the oil, but otherwise the results were very similar.

The effects of the extra digestion time on the observed nitrogen content of the shale was determined and found to be the same as with the shale oil. Also, as with the oil, the addition of sodium sulphate to the digestion mixture was necessary for the complete recovery of the nitrogen present. The results are given in Table 4.

TABLE IV.
Effect of Digestion Conditions on the Observed Nitrogen Content of Oil Shale.

(a) Without added Sodium Sulphate.

Additional Time of Digestion.	Observed Nitrogen Content Percentage.
Nil	0.623, 0.627
1 hour	0.678, 0.683
1½ hours	0.759, 0.760

(b) With added Sodium Sulphate.

Additional Time of Digestion.	Observed Nitrogen Content Percentage.
Nil	0.736, 0.808
½ hour	0.835, 0.845
1 hour	0.880, 0.869
1½ hours	0.896, 0.880
2 hours	0.889, 0.895
2½ hours	0.890, 0.899
	} 0.893 av.

DISCUSSION.

The only nitrogenous constituents of shale oil that have been identified are pyridine homologues; pyrroles are also present but no individual member of this series has yet been identified in shale oil (9). Other types of nitrogen compounds are most certainly present in the oil (10). At present practically nothing is known of the structure of the nitrogenous constituents of shale (11).

Shirley and Becker (6) found that, for the determination of nitrogen in pyridine type compounds by the Kjeldahl method, a total digestion time of three to four hours was required in order to obtain the full nitrogen value. Cole and Parks (12) found that pyridine type compounds required approximately three times as much digestion as other nitrogen compounds. In a study of the Kjeldahl determination of the nitrogen content of coal Beet and Belcher (13) isolated pyridine carboxylic acids from the products of the digestion and Beet (14) identified nicotinic acid among them. Woodward *et al.* (15) obtained yields of up to 76% of theory of nicotinic acid by the controlled Kjeldahl digestion of various β -substituted pyridine derivatives, and suggested the commercial application of the method.

These observations confirm the relatively slow oxidation of the pyridine nucleus under the conditions of the test and suggest that the analytical difficulty is a function of the high resistance of the pyridine nucleus to sulphonation. Other work at present in progress indicates that this property may allow the approximate determination of the amount of pyridine type compounds present in a material such as oil shale. On the basis of present data it is suggested that approximately 20% of the nitrogen present in the sample of shale examined is present in the form of pyridine rings.

SUMMARY.

The conditions have been determined for the accurate determination of the nitrogen content of shale oil and oil shale by the Kjeldahl method. A minimum digestion time of one and a half hours from the time the digestion mixture clears is necessary for the correct result to be obtained in both cases. This appears to be due to the presence of compounds containing pyridine nuclei.

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NITROGEN IN OIL SHALE AND SHALE OIL.

VI. ACID WASHING OF CRUDE SHALE OIL.

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INTRODUCTION.

The presence of organic nitrogen compounds has been found to have an important bearing on the behaviour of an oil towards catalytic cracking or hydrogenation. For example, Gordon (1) reports that the nitrogen content of a coal oil for hydrogenation must be kept below five parts per million in order to maintain a high activity for the tungsten sulphide hydrogenation catalyst.

Since all the nitrogen compounds that have been identified in shale oil in the past have been basic in character, the effect of an acid wash on the nitrogen content of the crude shale oil was examined to see if it could throw some light on the nature and distribution of the nitrogenous constituents of the shale oil.

COLD SULPHURIC ACID WASH.

Since sulphuric acid is the cheapest commercial strong acid, it was the natural choice, and its use was examined in detail. The acid was applied in varying concentrations and amounts. When using 5% to 10% w/v. acid the aqueous acid phase separated as such from the oil with a small amount of a tar. This enabled an estimate of the volume of the extracted tar bases to be made. When 25% w/v. or stronger acid was used the acid separated from the oil as a sludge.

EXPERIMENTAL PROCEDURE.

(a) *Washing Crude Shale Oil with 25% w/v. or Stronger Acid.*

Two hundred to 250 ml. of oil was measured into a separating funnel and the calculated amount of the sulphuric acid added. After two minutes' thorough shaking the mixture was allowed to settle for half an hour. The oil was then decanted, centrifuged and measured. Any sludge remaining in the separating funnel was drained into the centrifuge tube. With the thicker sludges this step was facilitated by warming the funnel to about 180° F. in an oven. After centrifuging the volume of sludge was measured. Traces of sludge left adhering to the separating funnel were disregarded.

With the concentrated (90%) acid a distinct temperature increase was obtained on contacting the acid and the oil. The maximum temperature increase in the acid phase was recorded, the temperature of the oil phase being approximately two degrees lower.

(b) *Washing Crude Shale Oil with 5% and 10% w/v. Acid.*

Cold Treatment. Two hundred to 250 ml. of oil was measured into a separating funnel and shaken for two minutes with the calculated amount of the acid. After settling for half an hour the spent acid was separated and centrifuged to remove traces of oil and tar before measurement. The washed oil was then centrifuged to remove traces of acid and tar before measurement. Tar

adhering to the sides of the separating funnel was liquefied by heating in an oven at about 180° F. for 15 to 20 minutes and then poured into the centrifuge tube for measurement.

The approximate volume of tar bases extracted from the oil was determined by rendering the filtered acid extract strongly alkaline with 40% caustic soda solution in a separating funnel that did not have very much air space. The liberated tar bases were extracted with 10.0 mls. of xylene and the volume of the extract measured in a burette after settling. The increase in the volume of the xylene was taken as the volume of tar bases liberated.

The results obtained using 5%, 25%, 50%, 75% and 90.4% (commercial concentrated) w/v. sulphuric acid are presented in Tables 1 to 5.

TABLE 1.
Treatment of Crude Shale Oil with Cold 5% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.*	Percentage Oil Recovered.	Sludge and Tar Percentage.	Tar Bases Percentage.	Nitrogen Content Percentage.
0	—	—	—	0.518
3	97.6	1.2	—	0.483
5	96.0	1.6	0.8	0.476
10	96.0	1.8	1.0	0.434
15	96.0	2.0	1.0	0.444
20	96.0	1.6	1.0	0.416

* 1 bbl.=35 imp. gals.

TABLE 2.
Treatment of Crude Shale Oil with Cold 25% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Nitrogen Content Percentage.
0	—	—	0.518
5	94.0	4.8	0.384
10	91.0	8.5	0.352
15	87.5	10.5	0.331

TABLE 3.
Treatment of Crude Shale Oil with Cold 50% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Nitrogen Content Percentage.
0	—	—	0.518
5	92.0	7.5	0.379
10	90.5	9.0	0.317
15	84.0	14.5	0.249

TABLE 4.
Treatment of Crude Shale Oil with Cold 75% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Nitrogen Content Percentage.
0	—	—	0.518
5	94.0	6.0	0.362
10	80.0	10.0	0.302
15	87.0	12.3	—

TABLE 5.
Treatment of Crude Shale Oil with Cold 90.4% Sulphuric Acid.

Pounds H_2SO_4 per Bbl. Oil.	Percentage Oil Recovered.	Sludge and Tar Percentage.	Temperature Rise ° C.	Nitrogen Content Percentage.	Sulphur Content Percentage.
0	—	—	0	0.518	0.66
5	91.4	9.8	6.1	0.303	0.68
10	87.2	15.2	8.9	0.156	0.78
15	82.0	20.4	10.7	0.150	0.72
20	80.4	24.0	11.2	—	0.64
25	79.2	26.0	13.8	—	0.60
30	78.0	27.2	14.0	0.104	0.59

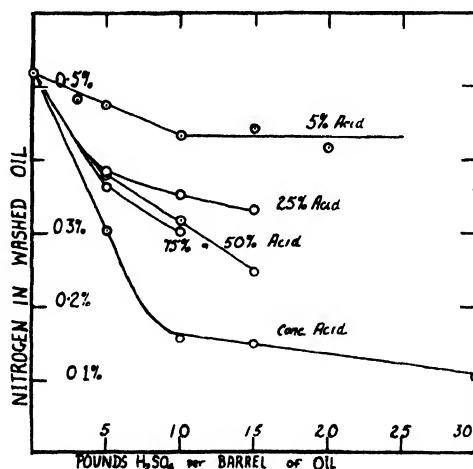


Fig.1.—Effect of H_2SO_4 Amount & Concentration on the Nitrogen Content of Crude Shale Oil.

These results indicate that at least three different classes of nitrogen compounds exist in the oil. The first class, which consists of the true tar bases and is extractable with dilute sulphuric acid, accounts for approximately 15% to 20% of the nitrogen in the oil. This small proportion of bases in the oil is in line with the observations of Bailey *et al.* (2), who found that very little of the nitrogen compounds in crude flow oils can be extracted with dilute acid.

The second class is not extractable with dilute sulphuric acid but is polymerized to give a heavy tar by the more concentrated acid, the tar being deposited as such or dissolved in the acid sludge. The 90% acid completely polymerized this class, while 5% to 10% acid had relatively little effect and the 25% to 75% acids were intermediate in effect. This second class probably consists of high molecular weight pyrroles or similar compounds which are readily polymerized by acids. It accounts for approximately 50% of the nitrogen in the oil.

The third class, which accounts for the residual 30% or so of the nitrogen in the oil, consists of non-basic, acid-stable compounds which are only sparingly soluble in the acid sludge, as shown by the slight but definite decrease in the nitrogen content of the residual oil on treatment with excess acid.

HOT SULPHURIC ACID WASH.

In a larger scale experiment to prepare a quantity of washed oil, 20 gallons of crude oil were added to a 44-gallon drum containing one gallon of concentrated sulphuric acid dissolved in 14 gallons of water. The drum was heated externally with a steam jet to reduce the viscosity of the oil for easier mixing and the acid contacted with the oil by passing a stream of compressed air through it for 12 hours. At the end of this time the oil did not discolour 5% sulphuric acid when shaken with it, so the extraction of the bases was considered to be complete.

TABLE 6.
Extraction of Bases from Crude Shale Oil.

<i>Crude Oil—</i>						
Total nitrogen before extraction	0.542%	N.	
Lab-washed with 5% H_2SO_4	0.428%	N.	
Drum washed with 5% H_2SO_4	0.346%	N.	
Sulphur content	0.56%	S.	
<i>Tar Formed—</i>						
Amount..	Approx.	4%	
Nitrogen content	1.94%		
Sulphur content	2.82%		

TABLE 7.
Treatment of Crude Shale Oil with Hot Dilute Sulphuric Acid.

Acid Strength. W/v.	Pounds H_2SO_4 per Bbl. Oil.	Treatment.	Per-centage Oil Lost.	Weight Percentage Tar and Sludge.	Volume Percentage Bases.	Nitrogen Content Per-centage.
—	—	Nil.	—	—	—	0.530
5%	5	Cold wash.	3½	n.d.	0.2	0.445
5%	5	Brought to boil.	1	1.15	0.2	0.408
5%	5	Boiled 5 minutes.	n.d.	1.0	0.2	0.414
5%	5	Boiled 10 minutes.	2	1.2	0.2	0.410
5%	5	Boiled 15 minutes.	3	1.25	0.25	0.426
5%	10	Cold wash.	3	n.d.	0.6	0.436
5%	10	Brought to boil.	3	1.4	0.5	0.420
5%	10	Boiled 5 minutes.	3	1.5	0.8	0.400
5%	15	Cold wash.	3	n.d.	0.5	0.420
5%	15	Brought to boil.	3	1.6	0.4	0.410
5%	15	Air passed.*	10	2.0	n.d.	0.420
10%	10	Brought to boil.	7	n.d.	0.8	0.414
25%	10	Brought to boil.	7	1.05%	0.7	0.322

* Air was passed five minutes before boiling. The oil was then brought to the boil and air passed for a further five minutes.

Examination of the treated oil (Table 6) showed that the "drum" treatment had reduced the nitrogen content by 0.196% against a reduction of 0.114% on washing with an equal volume of 5% sulphuric acid in the laboratory. Check analyses were carried out, but only confirmed these figures. On draining the drum a quantity of a heavy tar was obtained. This amounted to approximately 4% of the crude oil treated and its high nitrogen content (1.94%) accounted almost completely for the further reduction in the nitrogen content of the residual oil.

An attempt was then made on a laboratory scale to reproduce this result in the hope of finding the reason for the additional polymerization by the dilute sulphuric acid. The oil was boiled with varying amounts of acid for various lengths of time (see Table 7). This modification of the treatment was not successful though, with the boiling, as great a reduction in the nitrogen content was obtained with 5 lb. of acid per barrel of oil as with 15 lb./bbl.; whereas, in the cold, the larger amount of acid was slightly more effective. The boiling treatment caused the colour of the acid solution to become much stronger and darker than with the cold treatment.

Hot Treatment. Two hundred to 250 ml. of oil and the requisite amount of the acid were heated in a tared flask under reflux and the boiling continued for varying periods of time. When cold the volume of residual oil was measured as with the cold wash. The flask was rinsed with water, drained and allowed to dry before weighing to determine the weight of tar, all of which adhered to the glass.

It has been observed that crude shale oil deposits a solid product on atmospheric oxidation (3) and the analysis of such a deposit compares with that of the polymerization tar from the drum test, viz. deposit 2.23% N., 1.28% S.; tar, 1.94% N., 2.82% S.; crude oil 0.54% N., 0.56% S. It was therefore considered that the air used for stirring the drum could have been the active polymerizing agent. However, passing air through the boiling acid and oil in the laboratory gave no significant effect other than a somewhat greater oil loss from evaporation of the light ends in the air stream and a slightly greater tar yield (Table 7).

The use of boiling 10% sulphuric acid showed no improvement over use of the 5% acid. The nitrogen content of a sample of oil which has been brought to the boil with 25% sulphuric acid showed a significantly greater decrease. In this case two distinct tars were formed; one stayed between the oil and acid, where it gave difficulty in separation of the acid liquor, and the other (1.05%) sank below the acid.

The tar deposited in the flask in all the boiling tests was dissolved out in acetone and the solvent allowed to evaporate spontaneously. The acetone-free residue consisted of a mutually insoluble oil and tar. The oil contained 0.411% nitrogen, indicating that it was washed oil that had been entrained in the tar deposit. The tar contained 2.62% nitrogen, which suggests that the lower molecular weight compounds are the more readily polymerizable of the class and thus give rise to a greater nitrogen content of the tar.

OTHER ACIDS.

McKee and Parker (4) recommend the use of 25% acetic acid rather than dilute mineral acids for the removal of bases from oils. The effect of an acetic acid wash on the nitrogen content of crude shale oil was therefore examined. The acid concentration had relatively little effect on the results (Table 8), the residual nitrogen content remaining relatively constant with treatment with 10 pounds or more of acetic acid per barrel of oil. The acid and oil broke cleanly and there was no sign of tar formation with oil temperature below approximately 150° F.

TABLE 8.
Treatment of Crude Shale Oil with Dilute Acetic Acid.

Pounds Anhydrous Acetic Acid per Bbl. Oil.	Acid Concentration.		
	5% Acid Nitrogen Content Percentage.	10% Acid Nitrogen Content Percentage.	25% Acid Nitrogen Content Percentage.
Nil.. ..	0.621	0.621	0.621
3 lb. . . .	0.597	0.608	0.600
6 lb. . . .	0.557	0.558	0.562
10 lb. . . .	0.564	0.583	0.574
15 lb. . . .	0.576	0.578	0.573

TABLE 9.
*Treatment of Crude Shale Oil with Dilute Acids (Two Volumes of Acid
Used to One Volume of Oil).*

Acid Used.	Acid Strength.	Nitrogen Content Percentage.	Nitrogen Decreased Percentage.	Remarks.
None.	—	0.609	—	
Acetic.	25%	0.529	0.080	No tar formed.
H ₂ SO ₄ .	1.0 N.	0.500	0.109	Some tar formed.
HCl.	1.0 N.	0.419	0.190	Appreciable tar.
HNO ₃ .	1.0 N.	0.360	0.249	Large amount of tar.

Further tests were carried out to check the action of various acids on the removal of nitrogen from crude shale oil. It was found that the acids examined could be placed in the following order of increasing activity: acetic, sulphuric, hydrochloric and nitric acid (Table 9). The nitrogen-removing activity of the acids was paralleled by their tar-forming activity, acetic acid giving no tar and nitric acid giving a large amount. Accurate measurement of the tar formed was not practicable, so only the qualitative result was recorded, as this was quite satisfactory for purposes of comparison.

It is suspected that the greater polymerizing activity exhibited by the nitric acid may have been due, at least in part, to its oxidizing power, though this would not be great in the normal solution used. The use of this acid, however, failed to achieve even a 50% reduction in the nitrogen content of the oil.

DISTRIBUTION OF NITROGEN IN OIL.

A sample of crude shale oil that had been carefully vacuum fractionated (1 mm. mercury abs.) in connection with some other work was examined. The nitrogen content of the various fractions was determined both before and after washing with 5% sulphuric acid. Unfortunately insufficient sample was available for the cuts to be washed with concentrated acid as well.

The results (Table 10) show that both the total and the non-basic nitrogen compounds increase with the boiling point of the fraction. The basic or extractable nitrogen content increases to a maximum in the 500–600° F. cut and then falls steadily. It is interesting to note that less than half the nitrogen content of the fraction boiling in the gasoline range (to 360° F.) is sufficiently basic to be extracted with 5% sulphuric acid. Unfortunately insufficient amounts of the samples (only 5 to 20 c.c.) were available to determine the loss of oil on washing with the acid. Also the original oil and the distillation bottoms had been discarded and so could not be examined for their nitrogen content. However, the nitrogen content of the original oil could be taken as approximately 0.57% by analogy with similar samples. Since 0.32% of nitrogen (based on the total oil) has been accounted for in the oil distillate, 0.25% has to be accounted for in the distillation residue, which would therefore contain 2%.

TABLE 10.
Nitrogen Content of Crude Oil Fractions.

Boiling Range.	Fraction in Cut.	S.G. at 60° F.	Nitrogen Content.		
			Total.	After Acid Wash.	Decrease.
To 360° F.	14.2%	0.758	0.106	0.058	0.048
360–500° F.	9.9%	0.812	0.152	0.071	0.081
500–600° F.	13.0%	0.849	0.276	0.100	0.176
600–700° F.	13.5%	0.879	0.414	0.246	0.168
700–800° F.	18.1%	0.903	0.580	0.432	0.148
800–900° F.	18.7%	0.926	0.708	0.579	0.129
Bottoms	12.6%	(By difference)			

Nitrogen content of distillate on basis of original crude oil—

Total nitrogen 0.321%

Nitrogen after acid wash 0.223%

Decrease 0.098%

Nitrogen content of original oil 0.57% (est.)

Approximate nitrogen content of residue 2.0% (est.)

Horne, Finley and Hopkins (5) observed the decomposition of secondary amines from shale oil to give ammonia and tertiary amines on distillation, but the evolution of ammonia was not observed during the distillation of this oil. The bases extracted from the crude oil fractions by dilute sulphuric acid account for 0.098% of nitrogen in the original sample. This is of the same order as the amount removed from the unwashed oil by the same treatment. Therefore, unless, as seems most unlikely, the distillation residue contained a very high proportion of tar bases, it appears that the use of the high vacuum successfully inhibited this decomposition of the secondary amines.

EFFECT OF THERMAL CRACKING ON THE NITROGEN IN THE OIL.

The nitrogen content of various fractions of products from the Dubbs thermal cracking point was then investigated in order to determine the effect of thermal cracking on the nitrogen in the oil. In a parallel with the observations on the crude oil the nitrogen content of the fractions increased with the boiling point of the fractions, the residuum and coke containing over 1% of nitrogen (Table 11).

TABLE 11.
Nitrogen Content of Dubbs' Fractions.

	Total Nitrogen.	Nitrogen after Acid Wash.	Percentage of Contained Nitrogen Soluble in Acid.
Typical crude oil charge ..	0.52%	0.42%	19
Heavy recycle oil ..	0.684%	0.375%	45
Light recycle oil	0.470%	0.103%	78
Cracked naphtha	0.283%	0.048%	83
Residuum	1.042%	—	—
Coke—			
8.25% V.M.	1.502%	—	—
1.0% V.M.	1.033%	—	—

Residuum contained 1.04% nitrogen and a sample of coke that had been strongly heated in the laboratory until the volatile matter content had been reduced to 1% contained only 1.03% nitrogen, whereas a sample of normal coke containing 8.25% volatile matter contained 1.50% nitrogen. This indicates that a large proportion of the nitrogen in the crude shale oil, probably that observed to remain in the bottoms on vacuum distillation, accumulates in the residuum. On cracking to coke this nitrogen remains behind in the coke with normal operation but, should the coking conditions be intensified part of it is then split off.

The fraction of the total nitrogen content of the different cuts that could be extracted with 5% sulphuric acid decreased with increase in the boiling point of the cut but was, in all cases, much higher than in the raw crude oil. This indicates that the "non-basic" nitrogen compounds in the crude had probably been, at least partly, converted to true tar bases under the cracking conditions. This effect is parallel to the observations of Bailey *et al.* (2) on the conversion of the initially non-basic nitrogen compounds in crude flow oil to tar bases on cracking.

The presence of relatively large amounts of ammonia and traces of hydrogen cyanide in the cracked gases (6) indicate that appreciable and far-reaching decomposition of some of the nitrogen compounds had taken place.

OTHER OILS.

Some samples of shale oil produced in different manners were examined. These samples included oils produced from different shales on a commercial scale by various firms, and oils produced from Glen Davis shale in various manners. A sample of flow oil from Lakes Entrance (Victoria) was also examined and is included for comparison.

The results presented in Table 12 show that the range of the nitrogen contents of oil from Glen Davis shale is much smaller than the total range observed with the oils from various sources. At the same time a much larger proportion of the nitrogen from the other shale oils is acid-soluble. This applies to the oil from the N.T.U. retorts of Lithgow Oil Pty. Ltd., which have been claimed to give less cracked oils than the Fell retorts as used by National Oil Pty. Ltd. If this is so factors other than the thermal history of the oil are important in determining the nature of the nitrogen compounds in the shale oil.

TABLE 12.
Nitrogen Content of Shale Oils from Various Sources.

Producer.	Shale Source.	Nitrogen Content Percentage.		Remarks.
		Total.	Acid Washed.*	
Lithgow Oil Pty. Ltd.	Marangaroo.	0.792	0.486	Very little tar.
Mudgee Motor Fuels.	Peter's Creek.	0.810	0.547	Very little tar.
	Peter's Creek.	0.168	—	
Lewgil Oil Co.	Torbane.	0.627	0.398	Approx. 10% tar and sludge.
N.O.P. (No. 1 Bench).	Glen Davis.	0.518	0.42	Tables I and V.
N.O.P. (No. 2 Bench).	Glen Davis.	0.609	0.500	Table IX.
N.O.P. Grey King Assay.	Glen Davis Retortables.	0.549	—	—
N.O.P. Grey King Assay.	Glen Davis Main Seam.	0.603	—	—
		0.526	0.406	—
Benzol extract of Main Seam shale.	Glen Davis.	0.600	—	—
Lakes Entrance, Victoria.	Flow oil.	0.094	0.069	—

* Washed once with an equal volume of cold 5% sulphuric acid and centrifuged to remove suspended acid.

DISCUSSION.

The nitrogen compounds present in crude shale oil fall into three classes. The first class consists of basic nitrogen compounds which may be extracted with dilute acids. These bases are probably all pyridine type bases such as have been isolated from shale oils by several workers. Quinoline homologues may be present, though none have been identified with certainty in shale oils and they may be considered as pyridine type bases for the present.

The second class consists of the dilute-acid-insoluble nitrogen compounds which are polymerized by strong acids. This description tallies with the properties of the pyrroles which are very feebly basic and are readily polymerized in the presence of strong acids. Pyrroles have been detected as a class in shale oils by several workers, but no individual member of the series has, as yet, been isolated and identified. The degree of substitution of the pyrrole nucleus affects the stability towards acids, and this fact could readily explain the different degree of polymerization by the different acids and different acid concentrations. The possibility that other types of nitrogen compounds may be present here must not, however, be overlooked.

The third class of nitrogen compounds is stable to concentrated sulphuric acid and is not appreciably extracted by it, though some partition between the oil and acid appears to take place. Possible types of nitrogen compounds that could be expected to have these properties are the oxazoles, diazines, carbazole, etc. It is not considered likely that di- or triphenyl-amines, which would give comparable reactions, would be present in the crude shale oil, though the presence of the heterocyclic nitrogen compounds with two or more hetero atoms in the molecule are considered as likely to be present.

The increased proportion of the nitrogen that is present as tar bases in the partially cracked oils is in agreement with Bailey's observations (5) with flow oil that the non-basic nitrogen compounds give rise to tar bases on cracking.

The oil from the N.T.U. retort is normally considered to have been subjected to less secondary cracking than the oil from the Fell or other retorts. The higher proportion of tar bases in this oil either confutes this or some other factor must be operating. This other factor may well be that the much higher temperature reached in the combustion zone in the N.T.U. retort, which is above the oil distillation zone, decomposes to tar bases some of the nitrogenous materials in the shale residue which is passed out as such from the Fell retort. This suggestion is supported by the fact that approximately 50% of the nitrogen originally present in the kerogen is left in this shale residue. If this does happen both the total nitrogen and the tar base content of the oil would be increased by these additional bases.

SUMMARY.

The nitrogen compounds in crude shale oil have been shown to fall into the three classes :

- (1) Tar bases, which may be extracted by dilute acid.
- (2) Dilute-acid-insoluble but acid-polymerizable compounds.
- (3) Compounds stable towards and not extractable by concentrated sulphuric acid.

Twenty-five per cent. acetic acid will extract the tar bases without significantly affecting the second class, while dilute (normal) mineral acids cause some polymerization of the second class at the same time.

The total nitrogen content of the crude shale oil increases with the boiling point. The tar bases increase to a maximum (% N.) in the 500-600° F. fraction and then decrease again but, even with the gasoline fraction, they contain but part of the total nitrogen present in the fraction.

On thermal cracking the fraction of the nitrogen in various cuts appearing as tar bases increases. A large proportion of the nitrogen in the oil remains in the residuum and coke. The nitrogen content of shale oils from several different sources has been examined.

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NITROGEN IN OIL SHALE AND SHALE OIL.

VII. DISTRIBUTION OF KEROGEN NITROGEN ON CARBONIZATION.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., M.Inst.Pet.



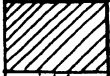


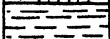

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INTRODUCTION.

In order to obtain further background information regarding the nitrogen in oil shale and shale oil the distribution of the nitrogen of the kerogen on carbonization was examined.

Firstly it is necessary to describe the shale seam itself. The shale mined at Glen Davis comes from two composite seams which are mined and retorted together. The accompanying figure gives a detailed cross-section of the seam. Both the relative thickness and richness of the various portions of the seam vary throughout the deposit, but the various bands retain their identity throughout the deposit.

Glen Davis Shale Seam.

thick.	SEAM	Sp. Gr.	ASSAY (gals per ton)
	1½" COAL	1.86	25
	4" "BLACKS"	1.88	37
	8" "GREYS"	2.30	17
	7" "WHITES" (STONE)	2.63	NIL
	7" TORBANITE	1.39	108
	7" "	1.20	140
	8" "	1.10	137
	7" "	1.18	168
	8" "	1.15	155
	5½" CANNEL	1.36	88
	8" TORBANITE	1.10	175

SEAM SUBDIVIDED FOR SAMPLING

Sample Nos. M294-M305.

TABLE 1.
Examination of Shale.

	Main Seam.		Secondary Seam.		
	Torbanite.	Cannel.	"Blacks."	"Greys."	Coal.
Proximate analysis of dry shale—					
Volatile matter ..	49.0%	43.2%	22.4%	18.0%	19.8%
Fixed carbon ..	18.1	27.0	7.0	1.0	26.8
Ash	32.9	29.8	70.6	81.0	53.4
V.M./F.C. ratio ..	2.7	1.6	3.2	18.0	0.74
Kerogen content of shale (a)	67.1	70.2	29.4	19.0	46.6
Kerogen content of shale (b)	—	68.8	24.9	12.0	43.6
Distribution of products on carbonization—					
Crude oil percentage by weight ..	54.0	23.2	10.5	2.8	7.7
Coke percentage by weight	40.75	72.5	75.1	86.1	83.9
Water distillate percentage by weight {	6.25	1.5	4.5	7.0	3.0
Ammonia plus loss percentage by weight {		1.8	9.9	9.9	5.4
Ash content of coke percentage by weight	56.5	47.2	88.9	93.9	58.9
Organic content of coke percentage by weight	43.5	52.8	11.1	6.1	41.1

(a) Assuming shale=kerogen+ash. This does not allow for the presence of the inorganic "retained" water in the shale, which is therefore reported as kerogen here.

(b) Assuming shale=kerogen+ash+"retained" water. The water obtained on retorting is here assumed to all be "retained" water which is also not strictly correct.

WORK DONE.

Samples of the different types of constituents of the shale seam were examined to determine the amount of nitrogen present and its distribution on carbonization.

The torbanite and the cannell were carbonized in the Gray King furnace to 600° C., while the blacks, greys and coal were carbonized to 600° C. in a one pound retort in order to obtain sufficient oil for testing. The yields of the various products of carbonization are recorded as percentages by weight of the charge. The samples were also characterized by proximate analysis (Table 1).

The distribution of the kerogen of each sample on carbonization was calculated from the nitrogen content of the raw shale, the coke and the crude oil. The analyses were carried out by the method previously described (2). No attempt was made to determine the amount of ammonia formed during carbonization so it is included with that small amount of the nitrogen liberated as elemental gas as "ammonia plus loss". The results of the nitrogen distribution are given in Table 2.

The oils were washed with an excess of 5% sulphuric acid and the nitrogen content of both the washed and unwashed oils determined. There was insufficient of the samples for the volume of bases extracted to be determined. However, the decrease in the nitrogen content of the oil after washing could be taken as a measure of the amount of tar bases formed. The acid wash of the oils from the

TABLE 2.
Nitrogen in Shale.

	Main Seam.		Secondary Seam.		
	Torbanite.	Cannel.	"Blacks."	"Greys."	Coal.
Nitrogen contents percentage by weight—					
Shale	0.726	1.080	0.254	0.080	0.945
Coke	0.920	1.330	0.198	0.070	0.986
Crude oil	0.526	0.662	0.616	0.554	0.924
Crude oil after washing with 5% sulphuric acid	0.406	0.461	0.456	0.381	0.386
Tar	—	—	Formed	—	1.245
Kerogen	0.96	1.53	0.86	0.89	2.03
Organic ash-free coke	2.12	2.56	1.79	1.15	2.40
Distribution of nitrogen on carbonization—					
Percentage in residue	51.5	89.3	58.8	75.0	87.5
Percentage in crude oil	39.0	14.2	25.6	1.9	7.5
Percentage in ammonia and loss	9.5	3.5	15.6	23.1	5.0
Percentage as tar bases	8.8	4.7	6.7	0.6	?
Percentage as non-basic compounds in oil	30.2	9.5	18.9	1.3	Tar* 1.9 } 6.1 }
Percentage extractable nitrogen in oil ..	25.0	31.0	35.0	32.0	—

* Assuming oil gave 40% of tar on washing with acid.

main seam shale, the cannel and the "greys" gave slight traces of tar and quite an appreciable amount of tar was formed from the oil from the "blacks". The oil from the coal gave approximately 40% by volume of a fairly hard tar, sufficient of which was available for its nitrogen content to be determined. As with the acid polymerization tars from the crude shale oil, the nitrogen content of the tar was higher than that of the oil (1).

DISCUSSION OF RESULTS.

It will be noted that the V.M. : F.C. ratio of the cannel is intermediate between those of the coal and of the torbanite and other portions of the seam.

This confirms the previous classification given to the various sections of the seam. The abnormally high V.M. : F.C. ratio of the "greys" is due to the large amount of water which is retained and chemically bound by the mineral constituents of the shale, being recorded as "volatile matter" in the test.

For the purposes of reporting the nitrogen contents of the kerogen the shale has been assumed to consist only of ash and kerogen. This is not strictly correct as the ash obtained by burning off the kerogen is not the same as the mineral matter in the shale. The inorganic minerals in shale are frequently hydrated and do not lose the water of hydration by heating just to 105° C. On ignition this water is given off and thus changes the composition of the inorganic constituents of the shale; this is particularly so in the "greys". In connection with this point carbonates such as calcium carbonate liberate carbon dioxide on

ignition if present and thus decrease the ash content of the original inorganic matter in the shale. Fortunately there is little if any carbonate in the Glen Davis shale.

The organic constituents of the shale or kerogen also tend to give some water of decomposition on carbonization, so it is not correct to take the water condensed in the carbonization assay as inorganic "retained" water, though it probably comes mainly from this source. The kerogen contents of the shales have been calculated on both of these bases for comparison (Table 1) but the nitrogen content (Table 2) has been based on the initial assumption that the shale consists of ash and kerogen only.

The calculated nitrogen contents of the kerogens on this basis are most interesting. The kerogens of the main seam, torbanite the "blacks" and the "greys" have approximately the same nitrogen content (0.96%, 0.86%, 0.89% respectively), while the cancell coal (1.53%) is intermediate between the shales and the coal (2.03%).

The nature of the organic precursors will naturally influence the final nitrogen content of the different sections of the deposit.

Since the nitrogenous materials concentrate during the formation of coal (3), difference in the nitrogen contents could possibly be taken as indicating that the shales have not been so fundamentally changed on "maturing" or weathering as the coal, and that the cancell coal has "matured" to an intermediate extent.

In each case over half the nitrogen of the kerogen remains in the coke.

It will be noted that the nitrogen contents of the ash-free portion of the coke of the blacks and greys are lower than for the other parts of the seam. These two samples also produced the highest proportions of water on carbonization. These two factors may well be connected as numerous workers have shown that the admission of steam to the carbonizing shale increases the yield of ammonia at the expense of the nitrogen content of the shale coke (e.g. 4, 5, 6, 7, 8). Unfortunately no explanation is available for the 103.5% recovery of the nitrogen in the cancell coal. The analyses were made in duplicate and the duplicates checked well.

The high percentage of the nitrogen from the "blacks" and the "greys" appearing as ammonia and loss may possibly be due to the factor mentioned previously, that the "retained" water converted some of the coke nitrogen to ammonia during the carbonization, though it would be expected that this effect would be slight.

On acid washing the oil from the coal, the acid was discoloured, showing the presence of tar bases. However, the oil gave a large amount of tar amounting to approximately 40% by volume. Using this figure with the respective nitrogen contents of the washed oil and tar accounts for 8.0% of the nitrogen of the shale as against 7.5% accounted for in the unwashed oil. This correlation is not the best but is as good as can be hoped for with the small samples available for examination.

With the other four oils the tar bases account for from 25% to 35% of the nitrogen in the oil. These figures are a little higher than those obtained earlier with commercially produced crude shale oil (1), but it will be noted that the nitrogen reduction by the acid wash was greater with the sample that gave the greatest amount of tar of the four. It is therefore likely that tar formation may be the explanation of the somewhat greater reductions obtained here.

For purposes of comparison the results of some other workers on the distribution of the nitrogen of shale on carbonization are given in Table 3 together with the results obtained in this work.

TABLE 3.
Distribution of Nitrogen.

Shale.	Reference.	Percentage Nitrogen Distributed in			Loss.
		Coke.	Oil.	Ammonia.	
Scottish	8	62.6	20.4	17.0	—
Scottish, distilled very slowly	8	45.7	20.0	32.8	1.5
American, in stream of hydrogen	6	21.0	24.9	49.0	5.1
Weimarn (U.S.S.R.) ..	7	—	—	5.5	—
Volga (U.S.S.R.) ..	7	—	—	18.9	—
Glen Davis—					
Torbanite	—	51.5	39.0	9.5	Ammonia plus loss for the Glen Davis samples.
Cannel	—	89.3	14.2	—	
"Blacks"	—	58.8	25.6	15.6	
"Greys"	—	75.0	1.9	23.1	
Coal	—	87.5	7.5	5.0	

SUMMARY.

Samples of shale from different parts of the Glen Davis seam have been examined and the distribution of the nitrogen on carbonization determined. Over half the nitrogen originally present in the shale remains in the carbonization residue.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge with thanks the assistance of C. J. Bray in carrying out this work, and the permission granted by the Management of National Oil Pty. Ltd. for the publication of this paper.

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THE LATE PRECAMBRIAN ICE-AGE AND GLACIAL RECORD OF THE BIBLIANDO DOME.*

By DOUGLAS MAWSON.

With Plates X-XIII and three text-figures.

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In doing honour to a pioneer of Australian geology on the occasion of this Clarke Memorial Lecture, I shall deal with a phase of geological enquiry not appreciated and explored in his day. At that time, geologists were already well acquainted with rôle of ice as a geological agent in eroding the face of the earth and in the accumulation in moraines of characteristic deposits resulting from such erosion. The key to the interpretation of such-like phenomena was furnished by the study of existing glaciers. It was later a comparatively simple matter to apply knowledge so gained to the elucidation of the record of the Pleistocene Ice-Age.

Then followed discovery of the evidence of extensive glaciation in late Palæozoic time. In this connection it is interesting to note that the first evidence of this ice-age discovered in this continent was made in South Australia by A. R. C. Selwyn in the year 1859. Later, in 1877, there followed Professor Ralph Tate's observation in the Hallett Cove area. This thoroughly aroused the interest of Australian geologists in locating further evidence of long past glaciations, and led to discoveries evidencing late Palæozoic glaciation, widely spread in Australia as well as elsewhere in the world.

Stimulated by these discoveries, geologists in South Australia eventually found evidence of a still more ancient glaciation, the first accepted record of Precambrian age. In this case the suggestion first came from H. P. Woodward in 1889, when accounting for a remarkable boulder rock met with near the northern end of the Flinders Ranges. Later, convincing proof of the existence of tillite in South Australian late Precambrian or early Cambrian strata was forthcoming in the year 1901 as a result of the field activities of Walter Howchin.

* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, July 15, 1948.

During the past 45 years, records of glaciation in past ages and distributed through many geological periods have come from all quarters of the earth. Apart from such as relate to the present Pleistocene-Recent Ice-Age, these testimonies of severe refrigeration are grouped in time, mainly about the closing stages of the Palæozoic era on the one hand and of the Precambrian on the other. It is now well established that in the Late Carboniferous and during much of Permian time, possibly extending over a period of 10 to 20 million years, our world lived through a glacial epoch greater in magnitude than that so far experienced in the present glaciation which, after all, has been in existence for a mere million years or so. Here in Australia evidences of late Palæozoic glaciation have been mounting up, until now sufficient to demonstrate that certain areas of this continent then supported ice-caps of great magnitude.

Still more remarkable is that, during the past 50 years, evidence of widespread glaciation in late Precambrian and eo-Cambrian times has been accumulating to such a degree that there can no longer be any doubt but that at that time, also, the world was in the throes of a severe ice-age. Evidence now forthcoming in South Australia, as a result of an extended study of the sedimentary record of that period, leaves no doubt as to the existence then of a vast land ice-cap in southern Australia, extending through a considerable period of time. The evidence for this conclusion is the main subject of my thesis this evening.

HISTORICAL.

Throughout a period of some 30 years, following upon his original demonstration of the existence of tillite interbedded among the more ancient strata of South Australia, Howchin continued to contribute accounts concerning the nature and extent of still further outcrops of this tillite which he designated the Sturtian Tillite, since it was first encountered by him in the gorge of the Sturt Creek near Adelaide. A list of such contributions appears in the bibliography incorporated herewith. During this long period Howchin traced the extension of this tillite over a very wide area in South Australia, a region some 400 miles in extreme length by 150 miles in extreme width.

This area was extended further to the east into western New South Wales by the author in 1906, firstly to Olary then to the Barrier Ranges, across the border (Mawson, 1909). Later, Jack (1915) reported what is apparently a reappearance of this tillite far to the north-west in the Everard Ranges. Subsequently, further details of occurrences within this area have been published by various authors. Mention of such is incorporated in the bibliography appended hereto.

At an early stage of investigation of the tillite and associated beds at Olary and in the Barrier Ranges, the author was convinced that the sedimentary record of this ancient glaciation is more complex, and extended through a longer period of time than indicated in Howchin's publications. Evidence of repeated advance and withdrawal of the ice was noted, and the glacio-fluvial origin of associated sediments was recognized. Thus in a contribution entitled "Extra-Glacial Sedimentation" read by me before the Association for the Advancement of Science in January, 1907, it was argued that the banded shales overlying the tillite at the Sturt Gorge and that of a lower horizon at Glen Osmond, both near Adelaide, was of glacio-fluvial origin. That contribution was in the nature of a discussion on the probable character of fluvial sediments deposited during an ice-age beyond the limits of the wholly glacial. In the views then advanced, I was assisted by an account of laminated glacio-lacustrine clays in Michigan by Berkey (1905) and by correspondence with Professor T. C. Chamberlin of Chicago, but, at that time, was unaware of the great work of Baron de Geer then in progress in Scandinavia. On that occasion, in illustration of the principles

laid down, it was held that on the basis of their petrological character, a considerable thickness of beds underlying the Sturtian tillite in the region of Adelaide, as far down as the laminated slates below the arkosic quartzite of Glen Osmond, were products of the ice-age period, thus advocating the earlier appearance of glacial conditions than that proved by the Sturt Gorge tillite itself. It was contended that the discovery elsewhere in South Australia of a tillite contemporaneous with the Glen Osmond beds might well be expected: the latter being regarded as the glacio-fluvial equivalent, beyond the actual limits of the ice. Publication of this paper was held over to permit of further elaboration and documentation. In search of first-hand knowledge of the conditions of sedimentation during an ice-age, it was then that the author welcomed an invitation to join an expedition (Shackleton's) proceeding to Antarctica.

It is obvious that little if any record of a great ice-age may ultimately be preserved on an elevated land surface subject to severe ice-cap glaciation. The complete historical document recording events during the progress of an ice-age can be preserved only in deep basins adjacent to elevated crustal blocks subjected to glaciation. In such places opportunity may be offered for the accumulation of an unbroken sequence of deposits embodying the complete story of the period represented.

Fortunately we have in South Australia an extensive geosynclinal basin whose initiation long preceded the oncoming of the late Proterozoic ice-age and which continued to receive sediments for a long period subsequent to its passing. Here, then, we have conditions most favourable for the study of sedimentation during the passage of that ice-age. In due course, it was discovered that the glaciogene sediments available for study in South Australia are much more complete than is offered in Antarctica, where the products of glacial erosion are almost entirely dumped on the floor of the surrounding ocean and thus not available for investigation.

As opportunity offered during very many years past, observations concerning these ancient glaciogene sediments of South Australia have been made until eventually, in 1939, the author succeeded in locating in the Bibliando Dome a long-sought opportunity to study an unusually complete and fully extended record of the sediments of that time. This investigation was completed in 1942 and has vindicated the views advanced in 1907 as stated above.

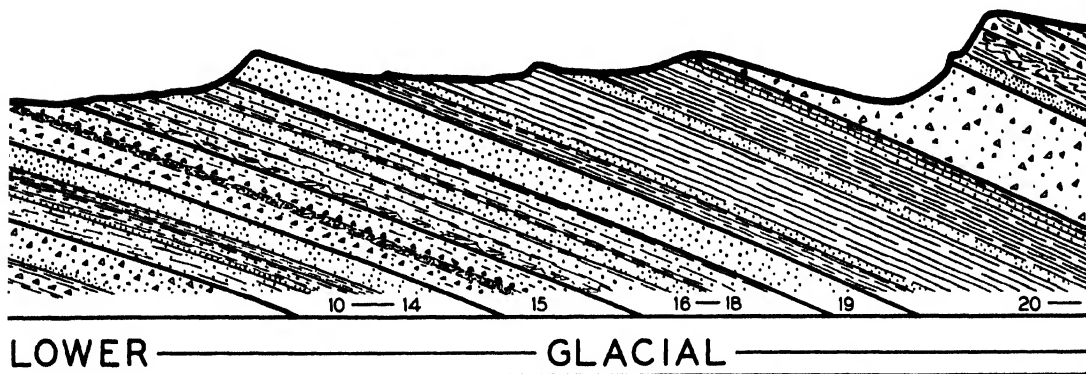
This great and deeply eroded structure, displaying an enormous thickness of strata, was located when investigating the more central area of the geosynclinal basin. The heart of the domed region is occupied by Bibliando Sheep Station; accordingly it is referred to as the Bibliando Dome. In it is exposed the most complete section of the glaciogene beds of the South Australian late Proterozoic succession yet encountered. In view of the great importance of this record to a discussion of the glaciation evidenced at that period and, further, in consideration of the value of such to the study of glaciogene sediments of a great ice-age, I am furnishing herewith a more than usually detailed account of the succession there exposed.

THE BIBLIANDO DOME.

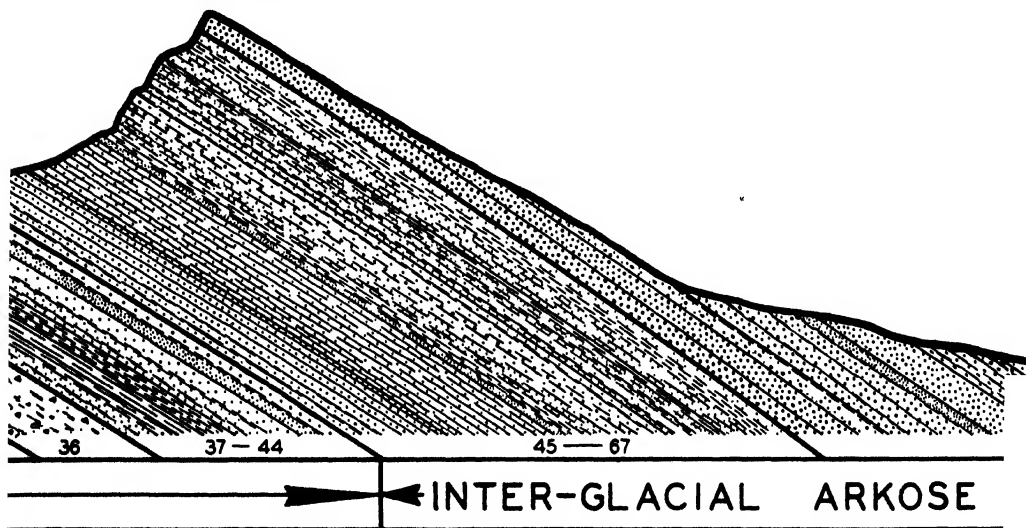
The topographical relief exhibited in the Flinders Ranges is primarily the result of differential erosion of the mass of sediments originally deposited in the Proterozoic-Cambrian geosyncline and later elevated as a folded mountain chain, the result of a Middle- to Late-Cambrian orogeny (Mawson, 1942, 1947). Subsequent peneplanation was followed by block elevation, apparently coinciding with the Kosciuskan period (Middle-Pliocene into Pleistocene) of displacements, which raised the region high above the surrounding peneplaned lowlands and permitted the inauguration of the present cycle of erosion which, in its turn, has

NORTHWARDS FROM CENTRE OF DOME

SCALE 0 100 200 300 400 500 YARDS



WILYERPA RIDGE



DEEP



accounted for the existing very striking topographic relief. Basins and domes are well exemplified in the structures illustrated. Of the former, Wilpena Pound is an outstanding example. Of the latter none is more perfect than the Bibliando Dome.

On page 153 is a plan of the Dome as plotted from aerial photographs of the region supplied by the Royal Australian Air Force. Scrutiny of the aerial photographs confirmed our ground reconnaissance in its finding of absence of faulting and serious distortion of the strata along the lines selected for geological section. However, the aerial photographs reveal notable disturbance of the strata immediately beyond the northern limit of our section.

Plate X is a vertical aerial photograph over part of the Bibliando Dome in the neighbourhood of Wilyerpa trigonometrical station (indicated by a white cross) and Bibliando Homestead (indicated by a white circular spot). This view illustrates the rugged nature of the country.

The centre of the Dome is situated approximately on a line joining Hawker and Silverton, about 42 miles east of Hawker and 58 miles north-north-west of Yunta. Willippa sheep station lies to the north of it; to the south is Baratta sheep station. Between the two is a high elevated region defined by a thick series of interglacial quartzites and arkoses encircling a central region occupied by soft, glaciogene sediments. Viewed from afar (Plate XI, Fig. 1) this great quartzite range with its remarkably accordant summit level limned against the sky is a really striking feature. Viewed from above, the elevated ring of quartzite surrounding the hollowed-out core region gives the impression of a gigantic crater. This latter is breached in three places by outflowing streams. One has broken through the southern wall along a crush zone, the result of faulting. Two others, travelling respectively in a north-easterly and easterly direction, break through the quartzite wall in its weakest section. Recently a homestead has been established within the crater pound, with access by way of the bed of the stream leading south through the shatter zone towards Baratta Station.

The highest point of the quartzite rim is known as Wilyerpa, but at a distance its superior elevation is scarcely noticeable. Wilyerpa rises to about 3,040 feet above sea-level. The lowest part of the pound floor is about 1,290 feet below the summit of the high ridge line. The low country encircling the elevated ring of quartzites, located some 1,600 or 1,700 feet below the highest point of the quartzite ridge, is occupied by a second great series of comparatively easily eroded glaciogene sediments leading on to lacustrine shales and limestones.

Plate XI, Fig. 2 is a view from just below Wilyerpa trigonometrical station, showing some of the periclinal quartzite ridges which constitute the elevated rim surrounding the central erosion basin—a domed pound.

The appearance of portion of the descent into the pound on the north side is illustrated in Plate XII, Fig. 1. There the strata inclines to the north at an average dip of about 28 degrees. A view across the centre of the Dome where the strata are horizontally disposed is illustrated in Plate XII, Fig. 2.

Details of a geological section extending northward across the strata of the Dome are tabulated below and further illustrated in graphic form against the surface relief in the folded page 154 herewith, where they are plotted approximately to scale.

It will be observed that this section was run in two divisions. The lower section from the centre of the dome to item 76 inclusive was measured along the line A-B as indicated in the folding map, on page 153. At B the line of section arrives at a flat alluviated region; consequently, in order to examine and record the upward extension of strata the line of section was then transferred to a hilly, well relieved belt of country some five miles to the west. There the sequence of beds recorded as items 77 to 188 inclusive was observed along the line C-D.

This line of section passes through Deep Well, a convenient camping centre where abundance of water is available. From Deep Well, Wilyerpa summit can be easily reached by an ascent of about 1,590 feet.

The stratigraphical succession listed herewith is set out in numerical order from below upwards, beginning in tillite in the centre of the Dome. The thickness of each of the recordings is the true thickness stated in feet. Bearings, where mentioned, are true, not magnetic. Names applied to sediments take consideration of their original unmetamorphosed form: thus such terms as shale and sandstone will be used notwithstanding that they may be in the state of slate or quartzite.

It is unfortunate that the Dome is not more deeply dissected and so permit the section to be extended completely through the entire record of that glacial epoch. However, as several boulders of magnesite were found in the creek bed downstream from this locality, originating in all probability as erratics in the tillite, it is likely that the section begins close to the base of the glacial series, for we have, in localities further to the west, for example at Mundallio Creek, observed magnesite erratics from the underlying formation in the basal portion of the tillite.

COMPLETE RECORD OF STRATA OF THE BIBLIANDO DOME.

(Stated in Ascending Order.)

Section along the line A-B.

	Feet
1. Grey, tillite with a large proportion of aqueo-glacial, rock-flour: containing erratics (granite, quartzite, gneiss), etc., up to 2 ft. diam. Horizontal to a 4° dip to the north	67
2. Tillite; near the base contains large erratics (to 30 ins.) but, above, only smaller boulders	26
3. Glacio-lacustrine rock-flour and silt rock with occasional bands of glacial grit	27
4. Outcrop obscured. Probably a soft rock-flour rock	57
5. A steep face of sandstone; soft and silty below to hard and laminated above	30
6. Glacio-lacustrine rock-flour rock with large erratics (to 15 ins.), the latter usually confined to certain horizons. Dip 4°	42
7. Glacio-lacustrine, rock-flour rock with a zone about 20 ft. in thickness, of large erratics (schist, quartzite, granite, red porphyry) commencing about 95 ft. from base of this item. The largest erratic observed was granite, measuring 6 ft. by 4 ft.	125
8. Sandstone. Strike N. 63° E.	3
9. Glacio-lacustrine, rock-flour rock with large erratics (granite, porphyry, quartzite, tourmaline, pegmatite, mica schist, chistolite schist) to 2 ft. diameter. A notable sandstone dyke cuts this section. Dip 10°	135
10. Glacio-lacustrine, silty to sandy rock-flour rock. No erratics observed	79
11. Laminated, quartz-rich arenite	2
12. Rock-flour rock with some zones notably sandy	70
13. Outcrop largely obscured by alluvium. The non-resistant underlying rock is probably sandy shale	23
14. Sandstone	86
15. Glacio-lacustrine, rock-flour rock with several horizons rich in erratics. One granite erratic 4 ft. diam. Intraformational puckering observed. Strike N. 64° E., dip 15°	190

Feet

16. Glacio-lacustrine, rock-flour rock with occasional sandy horizons of from a few inches to several feet in thickness. The lower limit is a laminated arenite with intraformational puckering ..	115
17. Sandstone	14
18. Rock-flour rock with arenaceous horizons. Slightly undulating. Dip 16°	146
19. Sandstone, especially hard at the base. Forms a ridge on the landscape	130
20. Rock-flour rock	75
21. Sandstone	15
22. Rock-flour rock	216
23. Sandstone	6
24. No observable outcrop. Apparently soft rock-flour rock	158
25. Rock-flour rock with interbedded arenaceous bands	63
26. A rock-flour rock with conchoidal fracture embedded in which at intervals are erratics (mica-schist and granite)	352
27. Sandstone	30
28. Rock-flour rock with some arenaceous horizons which vary in thickness from a few inches to several feet as a maximum. No erratics observed. The arenaceous horizons frequently exhibit bedding planes and contortions	136
29. Glacio-lacustrine, rock-flour rock with sandy horizons. Embedded are occasional mica-schist and granite erratics. Strike N. 70° E. Dip 20°. Outcrops along the top of a ridge	91
30. Sandstones and greywacke alternating with rock-flour silts	98
31. Chiefly rock-flour silty shales; minor interbedded sandstone horizons. Some small erratics and puckering	224
32. Chiefly silty, rock-flour shales with some erratics and puckering	140
33. Mainly arenites. Some interbedded silts and mudstones	117
34. Glacio-lacustrine, rock-flour bed; laminated and puckered in places. Occasional erratics	126
35. Dominantly arenaceous sandstones, siltstones and greywackes. Dip 24°	182
36. Mainly glacio-lacustrine, rock-flour shales with occasional erratics; puckering noted	252
37. Soft arenaceous and silty beds	85
38. Rock-flour rock with sandy bands more abundant near the base	20
39. Rock-flour rock for the most part exhibiting claystone fracture; sandy bands are rare	50
40. Alternating beds of rock-flour rock and arenite (the section here crosses a major creek)	64
41. Mainly hard sandstone but with some interbedded greywacke and rock-flour claystone. Dip 25°	130
42. Resistant sandstone	34
43. Sandy bands alternating with fine greywacke	20
44. Shaley glacial greywacke. Erratics appear at 30 ft. above the base of this section	44
45. Resistant sandstone	32
46. Soft sandstone	40
47. Resistant sandstone	12
48. Soft sandstone	60
49. Resistant sandstone	14
50. Soft sandstone	30
51. Sandstone	21

Feet

52. Sandy shale	128
53. Somewhat resistant arenaceous formation	11
54. Soft beds obscured by alluvium	41
55. Alternating sandstone and sandy shale. Sandstone beds each about 2 ft. thick	63
56. Sandy shale and some sandstone bars	35
57. Resistant quartzite. Dip 30°	20
58. Sandy shale	35
59. Quartzite	3
60. Fluvio-glacial claystone	15
61. Hard quartzite	8
62. Siltstone and shale with infrequent bands of sandstone	109
63. Resistant sandstone	5
64. Soft shaly beds	19
65. Soft sandy shale and sandstone covered by talus	68
66. Largely obscured by talus. Mainly slaty claystone and shale	45
67. Sandstone with surface covered by talus rubble	40
68. Quartzite. Outcropping on the ridge is a bold, almost vertical face. Strike N. 75° E., dip 31°	50
69. Mainly massive quartzite, but there are some thin silt bands in upper 20 ft. Normal bedding planes and current bedding are discernible though poorly marked	70
70. Gritty arkosic sandstone with some angular pebbles near the base but passing upwards into sandstone and siltstone, the latter increasing towards the top	60
71. Mainly sandstone and quartzite partly arkosic and siltstone intercalations in very minor amount	211
72. Strong quartzite, arkosic in part	119
73. Siltstone and feldspathic grit	132
74. Mainly quartzite, feldspathic in places, in four divisions separated by minor developments of softer siltstone and some feldspathic grit	376
75. Less resistant siltstone and grit	64
76. Siltstones and sandstone terminated above by a belt of hard quartzite	126

Section along the line B-C.

77. Laminated silt rock with occasional pebble bands; the latter more abundant near the top, where there is also a bed of sandstone 4 ft. thick. Strike N. 76° E., dip 25° to north	155
78. Flaggy to massive glacio-fluvial silts and sands more arenaceous near the base. Occasional pebble beds in which one quartzite erratic measured 18 ins. diameter	171
79. Glacial mudstones with some embedded erratics; less arenaceous in upper section	30
80. Somewhat arenaceous, laminated, glacio-lacustrine rock-flour flags with some grit bands	24
81. Arkosic sandstone with large erratics to 9 ins. diameter	3
82. Glacio-lacustrine mudstones to rock-flour flags with occasional bands of pebbles. Some contorted and swirl bedding observed. Strike N. 66° E., dip 24°	110
83. Unsorted glacio-lacustrine mudstone. No erratics noted	114
84. Rather arenaceous, glacio-lacustrine mudstone. No erratics observed	70

	Feet
85. Glacio-lacustrine mudstone and siltstone with only slight indication of lamination	39
86. Glacio-fluvial sandstone and siltstone with recurrent pebble bands..	93
87. Resistant arkosic sandstone	10
88. Laminated, silty rock-flour beds with some grit bands	140
89. Laminated and flaggy aqueo-glacial rock-flour rock; also siltstone and mudstone with some grit and small pebble bands	160
90. Laminated, rock-flour flags and siltstone with small-scale ($\frac{1}{2}$ in. to 12 ins. banding). Occasional bands contain small pebbles ..	101
91. Sandy and shaly glacio-lacustrine beds with occasional bands of unsorted glacial mud in which grit and some small erratics occur..	232
92. Glacio-lacustrine siltstone in which are occasional pebble bands suggesting concentration by current action. Dip 21°	57
93. Sandy mudstones with occasional bands of grit and pebbles	179
94. Banded, glacio-lacustrine mudstone and siliceous flags	84
95. Flaggy shales with grit bands	11
96. Tillite with medium sized erratics	16
97. Flaggy sandstone and grit beds	16
98. Sandy and slaty flags with some grit and occasional pebbles ..	149
99. Flaggy siltstones and sandstones with occasional small pebbles. Dip 20°	65
100. Gritty sandstone	41
101. Rock-flour flags and glacio-lacustrine unsorted muds	87
102. Flaggy grits and sandstones	123
103. Flaggy, glacio-lacustrine grits. Mainly fine-grained but frequent bands of coarse grit. Occasional large erratics	33
104. Coarse glacio-fluvial sandstone and grits	41
105. Finer grained, glacio-fluvial grits with interbedded horizons of tillite	103
106. Banded fine-grained, gritty sandstone	87
107. At the base, alternating glacial muds and gravels. Above, broader bands of coarser materials and some large erratics. Strike N. 85° E., dip 20°	154
108. Alternating flaggy glacio-fluvial, dense siltstones and grits.. ..	36
109. Flaggy, glacio-lacustrine muds and silts	20
110. Flaggy, glacio-fluvial, dense siltstones and sandstones	22
111. Glacio-lacustrine mudstones with occasional laminated bands. Also some bands each only a few inches thick of unsorted tillite..	40
112. Flaggy sandstone and mudstone	20
113. Alternating mudstones, grit and shales. Here have arrived at deep well. Dip 22°	37
114. Sandstone	10
115. Outcrops obscured by river flat alluvium. Probably soft, laminated, fluvioglacial shales	144
116. Varved shales exhibiting current wash in places. Alternating glacio-lacustrine grit and rock-flour. In this belt only occasional outcrops appear above the alluvium	215
117. Thin flaggy shale with occasional grit bands	77
118. Thin flaggy shale, fissile in part. Strike N. 77° E., dip 24°	114
119. Glacio-lacustrine shale, much of which is non-laminated	100
120. Flaggy glacio-lacustrine shale. Alternating bands of laminated and non-laminated rock-flour shale	146
121. Dense laminated shale	67
122. Resistant arenaceous shale	6

	Feet
123. Glacio-lacustrine grit and shale	28
124. Glacio-lacustrine sandstone	32
125. Glacio-lacustrine sandstone and mudstone	11
126. Shaly tillite with small erratics	34
127. Arenaceous glacial mud rock	60
128. Glacio-lacustrine grit and some erratic-bearing bands	68
129. Tillite	3
130. Flaggy slates	182
131. Glacio-lacustrine mud rock	11
132. Sandy glacio-lacustrine mud	18
133. Glacio-lacustrine mud	41
134. Dense, somewhat arenaceous shale	49
135. Shales more arenaceous below	46
136. Erratics in a sandy glacial mudstone	40
137. Dense somewhat arenaceous shale	38
138. Dense slates noticeable gritty below	42
139. Dense slates	69
140. Slate with a band of sandstone at the base	9
141. Slate with sandstone band at base	14
142. Tillite. Erratics of limestone and quartz	13
143. Slate	20
144. Slate with a 2 ft. thick band of sandstone at base	27
145. Slate with a 1 ft. thick band of sandstone at base	38
146. Slate with a 6 ft. thick band of sandstone at base	24
147. Shale with a 9 in. band of gritty sandstone at base	29
148. Shale with an 18 in. band of fine-grained arenite at base	29
149. Shale with a 12 in. grit band at base	12
150. Shale slightly calcareous at several horizons and a black grit band at base	73
151. Shales, faintly calcareous at certain horizons	115
152. Dense shales	105
153. Shale with some lamination. At base is a somewhat arenaceous band 12 ins. thick	143
154. Laminated shales. Strike N. 76° E., dip 19°	343
155. Flaggy shales with somewhat calcareous bands about 12 ins. thick recurring at the following intervals recorded stratigraphically upwards from the base: at the base, at 25 ft., 32 ft., 45 ft., 64 ft., 97 ft.	105
156. Moderately laminated, flaggy shale capped by a 6 ins. band of a bluish somewhat calcareous phase	20
157. Well laminated shale	65
158. Non-laminated flaggy shale suggesting original aqueo-glacial mud..	15
159. Poorly laminated shale	140
160. Flaggy laminated shale	11
161. Non-laminated flaggy shale, suggesting original aqueo-glacial mud..	28
162. Poorly laminated shale, with bands of a calcareous phase at the following intervals from the base of the section: 6 in. band at 66 ft., 19 in. band at 144 ft., 12 in. band at 164 ft... .. .	233
163. Well laminated shale with a 4 in. band of a calcareous phase at the base and an 8 in. band at 35 ft. above the base	85

	Feet
164. Laminated shales resembling the well-known occurrence at Tapley Hill (near Adelaide) but varying in degree of obvious lamination. At some horizons this shale is slightly calcareous. More notably calcareous bands were observed at the following intervals from the base up: 4 ins. thick at base, 15 ins. at 85 ft., 6 ins. at 120 ft., 15 ins. at 173 ft., 6 ins. at 240 ft., and 9 ins. at 725 ft.	905
165. Flaggy mudstone	23
166. Poorly laminated, flaggy somewhat calcareous shales with a notably calcareous band 9 ins. thick at the top	268
167. Flaggy, notably laminated, grey to blue-grey shales with interbedded bands of arenite (greywacke-sandstone) at the following intervals stated from below up: 4 ins. thick at base, 9 ins. at 104 ft., 9 ins. at 161 ft., 12 ins. at 538 ft., 6 ins. at 827 ft.	1,071
168. Poorly laminated shales with bands of greywacke at the following intervals stated from below up: 12 ins. at 286 ft., 36 ins. at 426 ft., and 18 ins. at the upper limit	471
169. Irregularly cleaving, somewhat calcareous slates. Dip 31°	384
170. Somewhat flaggy laminated shales with bands of greywacke at the following intervals stated from below up: 18 ins. at the base, 6 ins. at 39 ft., 12 ins. at 117 ft., 3 ins. at 167 ft., 3 ins. at 214 ft., 12 ins. at 271 ft., 3 ins. at 334 ft., 3 ins. at 357 ft., 9 ins. at 377 ft., 6 ins. at 387 ft., 3 ins. at 394 ft., 6 ins. at 398 ft., 18 ins. at 418 ft., 9 ins. at 474 ft., 12 ins. at 495 ft., 18 ins. at 533 ft., 12 ins. at 555 ft., 24 ins. at 564 ft., 18 ins. at 608 ft., 12 ins. at 612 ft., 6 ins. at 624 ft., 12 ins. at 647 ft., 18 ins. at 670 ft., 9 ins. at 688 ft., 6 ins. at 711 ft., 3 ins. at 735 ft., 6 ins. at 750 ft., 6 ins. at 784 ft., 6 ins. at 825 ft., 18 ins. at 859 ft., 6 ins. at 887 ft., 3 ins. at 906 ft., 6 ins. at 953 ft., 6 ins. at 977 ft., 12 ins. at 983 ft., 12 ins. at 1,001 ft., 6 ins. at 1,040 ft., 6 ins. at 1,092 ft., 6 ins. at 1,123 ft., 6 ins. at 1,150 ft., 6 ins. at top	1,167
171. Flaggy laminated grey shales	1,109
172. Greywacke with minor grey shale bands	302
173. Grey shales, very poorly laminated	138
174. Greywacke	5
175. Grey shale, very poorly laminated or without obvious lamination.	706
176. Greywacke	3
177. Grey shales and silty shales with some laminations	327
178. Resistant arenaceous shales	287
179. Grey slates partly laminated	345
180. Silty greywacke	12
181. Grey shales in part laminated	157
182. Greywacke	4
183. Grey shales. A 6 in. band at 100 ft. from base is calcareous	475
184. Resistant fine-grained greywacke	67
185. Grey shale and slate laminated in part only. A portion of this section exhibits slaty cleavage	1,733
186. Soft sandstone and sandy shales	139
187. Non-resistant beds under an alluviated area. Probably calcareous shale and limestone	438
188. Blue pisolitic limestone with bands of intraformational breccia. This corresponds to the Brighton limestone horizon of the Adelaide region	212
Total thickness of Sediment	23,125

SUMMARISED STATEMENT OF STRATA : BIBLIANDO DOME.

This remarkably thick series of sediments aggregating in all some 22,877 feet can be summarised by convenient assembly in cognate groups as set out below in descending order.

Calcareous, Lacustrine Shallow Water Deposits (Brighton Horizon) :
789 Feet.

Item	Feet
188. Blue pisolitic limestone with bands of intraformational breccia	212
187-186. Sandy and calcareous shales and some sandstone	577

Lacustrine Shales with Recurrent Bands of Greywacke : 8,763 Feet.

185. Grey lacustrine shales	1,733
184. Fine-grained greywacke	67
183-173. Shale, silty-shale and rare thin bands of greywacke ..	2,459
172. Greywacke with minor shale bands	302
171-167. Flaggy, laminated shales with recurrent thin bands of arenite..	4,202

Glacio-Lacustrine Shales and Minor Arenites : 2,856 Feet.

166-165. Flaggy, poorly laminated shale and mudstone	291
164-163. Laminated shales with some narrow calcareous horizons ..	990
162-150. Shale exhibiting varying degrees of lamination. Arenaceous intercalations on a very minor scale appear in the lower horizons, but are absent above where, however, slightly calcareous horizons make their appearance	1,396
149-143. Alternating beds of glacio-lacustrine sandstone and shale ..	179

The Upper Glacial Series : 4,556 Feet.

142. Tillite with erratics of limestone and quartz	13
141-137. Glacio-lacustrine sands and shales	172
136. Erratics in sandy mudstone	40
135-130. Glacio-lacustrine muds and sands	347
129-126. Shaly tillite and glacio-lacustrine grit and mud with small erratics	165
125-112. Glacio-lacustrine, flaggy banded and varved shales, siltstones, sandstones and grits	1,007
111-103. Flaggy glacio-lacustrine and glacio-fluvial series of mudstones, siltstones, sandstones, grits and pebble bands; with occasional thin bands of unsorted tillite	536
102-100. Flaggy glacio-lacustrine grits, sandstones and silts. No erratics observed	251
99-97. Flaggy glacio-lacustrine siltstone and sandstone with occasional small erratics	230
96. Tillite with medium sized erratics	16
95-94. Banded glacio-lacustrine muds, silts and sands	95
93-86. Glacio-lacustrine and glacio-fluvial muds and silts with recurrent bands of grit and small erratics	972
85-83. Glacio-lacustrine muds and silts. No erratics observed ..	223
82-77. Glacial and glacio-lacustrine beds with erratics	493

Inter-glacial Arkose and Quartzites : 2,062 Feet.

76-68. Resistant arkoses and quartzites with some minor silty partings	1,208
67-45. Glacio-fluvial sediments, mainly arenites with some minor silty and shaly bands	854

The Lower Glacial Series : 4,095 Feet plus.

	Feet
44. Glacio-fluvial silts and sands with erratics	44
43-37. Glacio-fluvial beds, sandstones, siltstones and shales ..	403
36. Glacio-lacustrine rock-flour shales with occasional erratics ..	252
35. Glacio-fluvial arenites, no erratics	182
34-31. Glacio-lacustrine beds with occasional erratics	607
30. Glacio-lacustrine arenites alternating with rock-flour silts ..	98
29. Glacio-lacustrine rock-flour silts with erratics and some bedded sandy horizons	91
28. Glacio-lacustrine beds. No erratics observed	136
27. Glacio-fluvial sandstone	30
26. Glacial rock-flour rock with erratics	352
25-20. Glacio-lacustrine alternating beds of rock-flour silts and sand- stone	533
19. Glacio-fluvial sandstone	130
18-16. Glacio-lacustrine rock-flour silts with minor bands of arenite ..	275
15. Tillite with erratics	190
14-10. Glacio-lacustrine shales, silts and sandstone. No erratics observed	260
9-1. Tillite and glacio-lacustrine rock-flour rocks with erratics ..	512
Total thickness exposed for observation	23,125

WARCOWIE-WILLIPPA ROAD SECTION.

At this stage it is appropriate to record that, at a point on the Warcowie-Willippa road 20 miles to the west of Deep Well, a further detailed section was run across the strike of portion of this same rock sequence.

The following is a highly summarised result giving only the thickness of the several main groups listed from above downwards :

	Feet
Pisolitic and sandy limestone (Brighton horizon)	—
Laminated shales and calcareous shale and impure limestone ..	1,688
Shales, laminated and unlaminated and minor arenite	3,341
Upper glacial beds and glacio-lacustrine shales	8,306
Inter-glacial quartzites	—
Total	13,335

This Warcowie-Willippa road section is actually a continuation of that already published (Mawson, 1941, p. 299) extending south from the Druid Range. Item (5), the pisolitic limestone of that section, corresponds to item (188) of the Bibliando Dome section, as stated in this paper ; it is also the ceiling below which the Warcowie-Willippa road section was measured.

In this more westerly line of section several disturbances (and possibly some faulting) were encountered at a stage shortly beneath the Brighton limestone horizon. Consequently the total of 13,335 feet is possibly an understatement of the true thickness. This thickness of strata located between the Brighton limestone horizon above and the great interglacial quartzite below is to be compared with the 16,752 feet of equivalent strata recorded in the Wilyperpa section. This is a decrease to the west of over 3,000 feet. Some increase in the more easterly locality is to be expected, since it is more central in the geosynclinal trough. However, obvious disturbance and faulting in the Warcowie section may account for at least some of the deficiency.

LITHOLOGY.

The range of glaciogene sediments represented in this record offers good opportunity for petrological studies. This phase of the investigation will, however, be reserved for another occasion. Attention will now be given only to some of the broader features.

In the case of the true tillites of this area, which are erratic-bearing rocks in which there is little if any evidence of bedding and where there is no evidence of sorting, the large proportion of fine rock-flour relatively to contained erratics is a notable feature. In all cases the rock-flour is coloured some shade of grey.

A number of erratics exhibiting faceting and glacial striæ were met with. Some thus striated were found actually embedded in the matrix. Except in the earlier deposits of the lower division of glaciogene sediments, their average size as met with here is less than in the case in some other localities that have come under observation in South Australia.

Of the more common rock types represented among the erratics may be mentioned granite, quartzite and various schists. They include both granite and chistolite schist corresponding so closely with similar rocks occurring *in situ* in the older Precambrian complex of the Olary-Outalpa region some 90 miles to the east as to provide convincing evidence of glacial transport from that direction.

Some horizons of otherwise normal tillite exhibit unmistakable evidence of deposition in water, in the nature of more or less well-defined bedding planes. In such cases accumulation may have taken place either in a lake or in the sea, the erratics having been transported by floating ice.

A not infrequent type of deposit is that where evidence of bedding planes is either meagre or wanting, and where the substance of the rock may be likened to a mud. Erratics are absent. In the field, I have regularly employed for such the awkward term "mother-of-till". This term was suggested, for we found that the appearance of such in the series invariably heralded the proximity of tillite.

In several locations, but more particularly interbedded with the tillites of the lower glacial series, there are formations of excessively fine and even grain-size, suggesting an æolian origin. It is difficult to account otherwise for the physical nature of these rocks. A glacio-æolian origin is more likely, as at times there is discernible no trace of bedding. In order to account for the characters exhibited in certain types of this kind of rock, I have been considering æolian transportation with final deposition in water.

A large proportion of the glaciogene beds possess a marked flaggy or laminated character. Where they are of pebbles, coarse gravel or grit alternating with bands of sand, silt or rock-flour, they have been interpreted as glacio-fluvial deposits. In these the banding is on a coarse scale, usually bands several inches to a foot in thickness.

At other times the alternations are of finer grained materials, such as bands of splintery sand alternating with silt or rock-flour. Such deposits are often of the true varve type and have been interpreted as glacio-lacustrine. Splendid examples of true varving are met among these ancient glaciogene sediments (Plate XIII, Fig. 1).

The coarse banded glacio-fluvial sediments are always closely associated in the series with true tillites. More remote from the tillites, the banding exhibited gradually passes into fine ribbon-like lamination so well exemplified by the Tapley Hill shale of the Adelaide region. The laminae in the case of shale of this nature commonly range from $1/8$ to $1/12$ inch in thickness. Their relation to seasonal deposition is still a matter for discussion, though as already

stated it was advocated by the author as such as early as 1907. These finely laminated silts and argillites are apparently the expression of peri-glacial deeper water depositions.

Shallow water peri-glacial sediments are of an arenaceous nature in which the grains are notably angular even to the extent of being splintery. When deposition has proceeded contemporaneously with adjacent glaciation these arenites are characteristically either of the arkose or greywacke type. Where deposition has proceeded at a time or place more remote from active glaciation the resultant rock approximates more and more to the character of normal sandstone.

Finally, a noteworthy feature frequently evidenced in these glacial beds is that of intra-formational disturbances of bedding (Plate XIII, Fig. 2). Crumpling and buckling of this kind are a frequent feature of the mud and silt rocks; occasionally they have been noted in the arenites. Among such features observed in our traverse of the Bibliando Dome some are of the nature of simple slump structures.

Lenses of fluvial sands are met with in certain of the tillite horizons. These which may be limited to a few yards in width and a few hundred yards in length appear to have originated as eskers.

The occurrence of one or more sandstone dykes up to four feet in width have been observed discordantly intersecting the glacio-lacustrine beds overlying the main tillite horizon of the lower glacial series.

ADVANCE AND RETREAT OF THE ICE FRONT.

The record of strata constituting the Bibliando Dome reveals the fluctuating character of sediments deposited in that area. Variation in the nature of the depositions must have been dependent upon several changing factors, more especially linked with (1) the advance and retreat of the ice front, (2) with periodic subsidences and elevation of the land in relation to sea or lake level, (3) the shallowing or deepening of the lake or sea in which some of the deposits were accumulated.

During the progress of the ice-age certain events with far-reaching concern to the progress of sedimentation must have operated: such as (a) isostatic movements of the land due to ice loading and unloading, and (b) eustatic fall and rise of the surface of the oceans following upon ice accumulation and dissipation.

Detailed reconstruction of the climatic and geographical history of the time, based on the changing character of the deposits at any one place, is, in view of the diverse factors influencing their nature, a most uncertain problem. However, the varying degree of glacial intensity recorded in the stratigraphical succession clearly indicates that there must have been frequent notable advances and recessions of the ice front, and this on a scale suggestive of inter-glacial periods.

Formations containing erratics, and therefore depositions at a time of notable ice activity, alternate with beds free from any convincing evidence of ice transport. It will be observed that these latter are, in a number of cases, each of such thickness as to represent deposits accumulated over a period of time of considerable magnitude, corresponding to the interglacial intervals of the Pleistocene. However, it is my view that until detailed corroborative observations are accumulated from many localities scattered throughout a wide geographical area, it would be rash to place reliance on the apparent climatic significance of such features appearing in this individual record.

There can be no doubt, however, that the thick arenaceous belt represented by items (45) to (76) inclusive were accumulated during a major interglacial

epoch. This accords with observations made at a number of localities in South Australia. Two such widely separated horizons of late Proterozoic tillite were met by me (as yet unpublished data) in the Olary district in 1907, Burra Creek west of World's End in 1922, at Pualco in 1932, and Jamestown-White Yarcowie in 1939. Such has also been recorded by Jack at Mt. Grainger (1916) and Dickinson at Burra (1941).

Segnit (1939), reexamining Jack's Mt. Grainger tillites, came to the conclusion that there existed only one tillite horizon, which had been repeated by faulting. This I have since checked and fine Jack's recording to be absolutely correct. In our investigation of the area we found some 8,000 feet of fluvial sediments separating the main tillite horizon at Mt. Grainger from the conformably overlying Dust Holes Range tillite.

The record at Bibliando clearly indicates two extended periods of glaciation separated by a notable interglacial epoch. The question arises as to which of these divisions of the glacial record should be regarded as equivalent to the tillite of the Sturt Gorge and therefore Sturtian in the full sense of the term. However, the fact that the Sturt Gorge tillite passed directly upwards through laminated slates to the Brighton Limestone horizon demonstrates its equivalence to the upper glacial sequence of the Bibliando section. To distinguish the lower record of extended glaciation we may refer to it as the Bibliando stage. Such knowledge as we already have of the Proterozoic succession over a wide area of the geosynclinal basin indicates that evidence of the lower, Bibliando stage of glaciation may be limited to the deeper portions of the basin. Any depositions in the marginal areas would tend to be stripped by the subsequent glaciation.

Some evidence of glaciation at a later date than recorded in the strata of the Bibliando Dome (actually located above the Brighton Limestone horizon) is now under investigation. If this can be sustained then even the thick series of slates and limestones of the uppermost part of the succession herein recorded may itself be interglacial.

EVIDENCE OF A MAJOR ENDURING ICE-CAP GLACIATION.

The systematic collection of erratics by the author from outcrops in many parts of South Australia and the Barrier Range in New South Wales has yielded proof that the ice at this period was in the nature of one or more ice-caps of great extent, transporting erratics at various times into the central basin from the region of Olary and the Barrier Ranges in the east, also from the vicinity of Mt. Painter to the north and from the Gawler Ranges far to the west.

Furthermore, the floor of portion of the basin itself, notably in the marginal areas, was actively eroded by the ice, the lower tillite in some areas being loaded with the debris of the underlying formations (Mawson, 1947). The nature of the basal tillite in relation to the underlying formation at a locality near Kapunda recorded by Howchin (1927) is further evidence of the overriding nature of the ice sheet. Andrews (1922, p. 65) also has given clear evidence of ice sheet erosion of the underlying rock formation. So far, however, there has been no discovery of a polished and ice-scratched basement.

Evidence now accumulated indicates that the scale on which the ice operated in South Australia implies a far greater geographical extension in the Australian region than that so far proved. Professor Carey's (1946) recent discovery of tillite, apparently of this same age, on King Island in Bass Strait, and near Zeehan in Tasmania, supports this contention.

THE STRATIGRAPHICAL POSITION OF THE BIBLIANDO TILLITES.

As already mentioned (p. 163), the upward succession of beds above the Brighton Limestone horizon, item (188) of the Bibliando Dome section, is to be found in an earlier publication (Mawson, 1941a), where a further thickness of

12,330 feet of sediments carries the stratigraphic column to the base of the Pound Quartzite, which can no longer be considered other than Cambrian. Briefly summarised, this succession is now stated in descending sequence :

Section Measured South of the Druid Range.

	Feet
Hard, white Pound Quartzite of the Druid Range, 2,470 feet.	
Soft, red sandstone, sandy shales and red shale	1,070
Flaggy shales, in part calcareous, also some bands of impure limestone	2,410
Upper Chocolate Series	1,690
A.B.C. sandstone	240
Flaggy slates with sandstone bars above	1,120
Middle Chocolate Series	2,550
Grey shales with some narrow, minor bands of arenaceous limestone	680
Lower chocolate series of shales with some narrow bands of limestone and a little soft sandstone	1,870
Flaggy calcareous argillites, and a little grey limestone ..	700
Oolitic, and in part arenaceous limestone with some crypto-zoonic markings	240

Section Measured Across the Bibliando Dome.

Calcareous arenaceous shales and some sandstones	577
Lacustrine shales with recurrent bands of greywacke	8,763
Glacio-lacustrine shales and minor arenites	2,856
Upper Glacial Series	4,556
Interglacial arenites (sandstone and arkose)	2,062
Lower Glacial Series (as far down as exposed)	4,095

Total thickness below the Cambrian Pound Quartzite..	35,479
--	--------

As already mentioned, the Lower Glacial Series is not expected to continue much below the lowest horizon recorded in the Bibliando section. In all probability, the immediately pre-glacial sediments in the area under discussion will be found to be shales with much dolomite and magnesite (Mundallio horizon) overlying thick sandstones (Emeroo Range horizon).

At Mundallio Creek (Mawson, 1947) closer to the margin of the geosynclinal basin, the tillite rests on an eroded surface of the underlying beds, and there remains below it only 7,453 feet of the latter above the base of the system. Near Copley (Mawson, 1941), 140 miles to the north, pre-glacial erosion appears to have been much less, for there exists below the glacials some 6,228 feet of the dolomite-magnesite series overlying the 5,217 feet of basal quartzite (Aroona Waters or Emeroo Range quartzite): total 11,445 feet. The Precambrian sediments of the great late Proterozoic-Cambrian geosynclinal trough of South Australia therefore in its thickest development amounts to not less than about 47,000 feet.

The term Adelaide Series, or better Adelaide System, was some 25 years ago proposed to signify the thick, virtually unfossiliferous sediments of this basin in the neighbourhood of Adelaide, extending upwards from the violently unconformable basal sandstones to the base of the fossiliferous Cambrian above. Howchin, however, adopted this term to include only the Brighton Limestone and underlying beds; he preferred, even to the last, to consider as Cambrian all beds between the Brighton Limestone and the fossiliferous Cambrian. To

further clarify Howchin's viewpoint it may be mentioned that in all his earlier publications he referred to the succession up to and including the Brighton Limestone as Lower-Cambrian, and to the beds above as Upper-Cambrian. At a later date he conceded that the Brighton Limestone and underlying beds might possibly be Precambrian, and he accepted the fossiliferous Cambrian as Lower-Cambrian.

The vast thickness (47,000 feet) of sediments in the region of Bibliando is representative of the northward extension of the Adelaide System. In the vicinity of Adelaide, Sprigg (1942 and 1947), reviewing Howchin's figure of 13,000 feet, states the thickness of strata, from the base to the quartzite counterpart of the Pound formation of the northern areas, to be about 23,000 feet. Even this is considerably less than its counterpart in the more central region of the basin.

It is noteworthy that in the Australian region, in late Proterozoic time, the climate passed from glacial to arid, as indicated by the chocolate shales of the upper portion of the Adelaide System. A similar development is recorded after both the late Palaeozoic and the Pleistocene glaciations. But Australia is no exception in this regard, as aridity is widely recorded following upon great ice-ages in other parts of the world. This is, indeed, so much the case that it can be considered an established sequence, which suggests that the application of the factor responsible for subsequent aridity was also concerned in the passing of ice-ages. The factor most obviously involved is of course reduced precipitation: what may have in time led up to this is not so obvious, and could conceivably be accounted for as the result of one or more of several controls.

AGE OF THE GLACIATION.

The glaciogene sediments recorded are interbedded in the Adelaide System, which is but little affected by regional metamorphism and, so, much resembles normal Palaeozoic sediments. They are, however, unfossiliferous. Howchin earlier maintained his Sturtian tillite to be of Cambrian age as it underlay, without an apparent break, though at a considerable depth, fossiliferous Cambrian strata.

Now, however, the odds are all in favour of the Sturtian glaciation, being of Proterozoic age; probably late Proterozoic. The main considerations that lead to this conclusion are:

1. The lower horizon of fossiliferous Cambrian strata in the basin is now regarded as of Lower-Cambrian age (David, 1932).
2. The lowest fossiliferous horizon, the Pound Sandstone, appears to disconformably overlie the subjacent beds.
3. The vast thickness of post-glacial sediments underlying the fossiliferous Cambrian implies a long period of time.

It is appropriate that some explanation and qualification be made to the assertion that the sediments below the Pound Quartzite are unfossiliferous. Actually, the limestones do contain abundant structures which have long been accepted by me as resulting from organic agency; these are the cryptozoonic forms now widely recorded in Proterozoic strata from many parts of the world. The view now widely advocated that such are the result of the biochemical activities of certain types of algæ has, for long past, been accepted by the author as the most probable explanation. These structures, however, in the present state of knowledge cannot be accepted as of chronological value.

Discoveries of radiolaria reported by Howchin and David and, later, of segments of crustacea reported by David have not been confirmed by other workers (see Sprigg, 1942, 1947).

In fact, no evidence has yet been forthcoming that clearly indicates a marine origin for any part of the Adelaide System. The facts are compatible with a continental origin as advocated by Grabau (1940) for the Sinian system of China and by Blackwelder (1932) for an extensive late Proterozoic System embodying tillite horizons widely extended in Utah and Wyoming.

In recent years a number of ancient tillites discovered in various parts of the world have been reported as of Cambrian age, a decision consequent upon the finding of Cambrian fossils in superimposed beds, though there may be a considerable thickness of unfossiliferous strata between the evidences of glaciation and the fossiliferous horizons. In some cases reexamination of the areas has revealed evidence of disconformity or nonconformity in the intervening strata. There has thus been a fairly general tendency to refer this glacial epoch back to the later Proterozoic. Aspects of this controversy have been well discussed by Oskar Kulling (1936), who has contributed greatly to the evidence available. There appears thus to be a clear case for major world-wide glaciation in the late Proterozoic, and the evidence forthcoming in Australia supports this conclusion.

How far back into the Proterozoic the glaciogene sediments of the Bibliando Dome extend is another matter. We have shown that the earlier tillite is some 35,000 feet below the base of the Lower-Cambrian. The accumulation of this thickness of sediment must signify the passage of a considerable period of time.

It is worthy of note that some of these late Precambrian tillites, as for example the Sturtian of Australia, the Griquatown tillite of South Africa (Du Toit, 1939) and the Sveanor tillite of Spitzbergen (Kulling, 1936), though geographically remote from each other, are constituents of sedimentary successions which exhibit certain notable correspondences; so much so that contemporaneity of their deposition is strongly suggested.

WORLD-WIDE NATURE AND MARKED INTENSITY OF THIS GREATEST ICE-AGE.*

Records of severe glaciation in the late Precambrian are fast accumulating. So far as can at present be judged, frequent and widespread refrigerations were a feature of at least middle to late Proterozoic time. Glaciation is evidenced even to the Equator itself.

Authentic records of such from beyond the limits of Australia are now known from India, China, Central Asia, Siberia, Finmark, Norway, Spitzbergen, North-east Greenland, Canada, Utah and neighbouring states, and many places in South and Central Africa. The accompanying sketch map (Fig. 3) roughly indicates their distribution.

SOME RECORDS OF PRECAMBRIAN GLACIATION.

(See Fig. 3.)

1. Sturtian tillite: South Australia and N.S.W. (herein discussed).
2. King Island tillite: King Island, Bass Strait (Carey, 1946).
3. Nantau tillite: China (Lee, 1924).
4. Blaini tillite: Himalaya (Holland, 1908).
5. Varogva tillite: Yenisei Range, Central Siberia (Nicolaev, 1930).
6. Kuten-Buluk Range tillite: Southern Siberia (Tchurakov, 1933).
7. Kuruk-Tagh tillite: Central Asia (Erik Norin: see Kulling, 1936).
8. Sveanor tillite: Heckla Hoek Formation, Spitzbergen (Kulling, 1936).
9. Bossekop tillite: Finmarken (Coleman, 1926; Kulling, 1936).

* When preparing this address I overlooked Professor B. F. Howell's contribution to the subject read before the International Geological Congress at Moscow in 1938. This important paper, a copy of which I have just received (Aug., 1948), is entitled: "Late Proterozoic and Early Cambrian Climates".

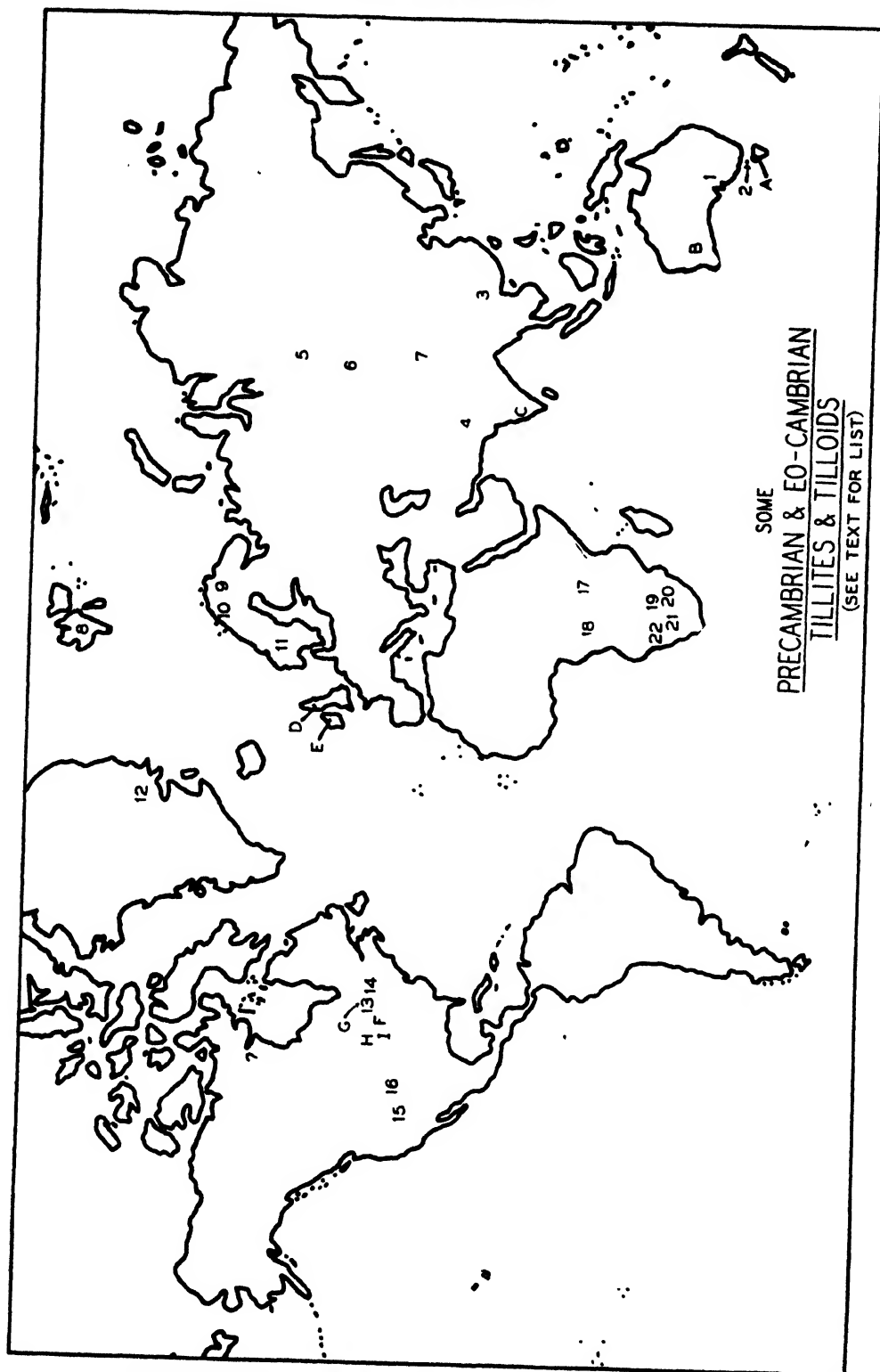


Fig. 3.—Some Localities where Precambrian Tillites or Tilloids have been Reported.

10. Varanger tillite : North Norway (Kulling, 1936).
11. Sparagmite tillite (Kulling, 1936).
12. Cape Oswald tillite : North-east Greenland (Kulling, 1936).
13. Bruce Series tillite (?) : Ontario (Coleman, 1926).
14. Gowganda tillite : Ontario (Coleman, 1926).
15. Utah tillites : Various occurrences in Utah (Blackwelder, 1932).
16. Medicine Bow River metatillites : Wyoming (Blackwelder, 1926).
17. Bunyoro tillite (?) : Uganda (Geol. Survey specimen submitted 1928).
18. Kundelungu tillite : Congo (Beetz, 1929).
19. Daspoort tillite : Pretoria Series, Transvaal (Du Toit, 1939).
20. Government Reefs tillite : Witwatersrand System, Transvaal (Du Toit, 1939).
21. Numees tillite : Transvaal System, Southern South-West Africa (Du Toit, 1939).
22. Chuos tillite : Damara System, South-West Africa (Du Toit, 1939).

Tilloids with Characteristics Suggestive of Glacial Origin.

- A. Zeehan tilloid* : Tasmania (Professor Carey, personal com.).
- B. Kanowna tilloid : Western Australia, (herein mentioned).
- C. Kaldrug tilloid : (Dharwar), India (Coleman, 1926).
- D. Gairloch tilloid : (Torridonian), Scotland (Coleman, 1926),
- E. Dalradian tilloid : Donnegal, Ireland (Coleman, 1926).
- F. Pointe aux Mines tilloid : (Keweenawan), U.S.A. (Coleman, 1926).
- G. Timiskaming tilloid : Canada (Coleman, 1926).
- H. Shoal Lake tilloid : (Seine Series), Canada (Coleman, 1926).
- I. Doré tilloid : (Keewatin), Canada (Coleman).

As for evidence of late Precambrian glaciation within the Commonwealth of Australia, reference has already been made to the region involved in South Australia and western New South Wales. Then there is Carey's (1946) recent discovery of tillite on King Island.

A more ancient period of glaciation is evidenced at Kanowna in Western Australia. There a tilloid meta-conglomerate associated with much laminated meta-argillites exhibits so many of the characters indicative of glacial origin that, after a very brief inspection in 1926, the author accepted it as such.

Nor is this all, for in South Australia also, proof of an older Precambrian glaciation has been gradually mounting and may soon be conclusive.

Verily, the Precambrian during at least its later stages was an era of marked glaciation. When allowance is made, firstly for the obliteration as the result of long-continued erosion of a very large part of such ancient formations, secondly for the limited areas of Precambrian strata exposed for inspection, thirdly for the fact that so much of such ancient formations has been metamorphosed out of recognition of its original character, then it must be conceded, in view of the abundance and wide distribution of Precambrian tillites already located, that glaciations of Precambrian time were probably the most severe of all in earth history ; in fact the world must then have experienced its greatest Ice-Age.

PROBABLE INFLUENCE ON THE RECORD OF PRECAMBRIAN LIFE.

As Grabau (1940, p. 65) states, " No one any longer questions the existence of life long before the time of the earliest Cambrian organisms that we have any record of. But the nature of the organisms, and the reason for the all but

* Now proved to be a Tillite.

complete absence of a record of their existence has been one of the major puzzles of our science."

It is universally conceded that the sea is the mother of life and that all early evolutionary development proceeded in the sea. If as has been advocated, the volume of the hydrosphere was materially less in Precambrian times than in succeeding ages, the elevated sialic continental areas must have stood notably high above the primordial ocean-filled basins, where alone records of contemporary life could be preserved.

The severity and long duration of the period of refrigeration preceding the Cambrian must have exerted a profound influence upon evolution and the distribution of life of that time. Limitations imposed by glacial conditions may well have been an important factor in confining life to narrow geographical regions, the sedimentary records of which have never yet been discovered: perhaps lost beneath the present expanded oceans or deposited in such zones as have been deeply depressed and overwhelmed in crustal revolutions the sediments themselves perhaps paligenetically reconstructed.

Then with the advent of Cambrian time and the melting of ice-caps, shallow epiiric seas rich in life spread over the continental lowlands to deposit the first great record of marine life.

SUMMARY.

The Precambrian sedimentary record of the central region of the late Precambrian to Middle-Cambrian geosynclinal basin of South Australia, as deduced mainly from measurements made across the Bibliando Dome, is detailed and is shown to amount in all to close on 50,000 feet.

Special attention is paid to the glaciogene section of the record; this is shown to have accumulated in two main divisions separated by a notable interglacial epoch.

Evidence is given of large-scale ice-cap glaciation in Australia during the late Proterozoic. Records of glaciation at this same time are quoted from other parts of the world; these also indicate extensive and severe glaciation. Attention is drawn to the effect of such climatic extremes upon evolution and the distribution of life during Precambrian times.

ACKNOWLEDGEMENTS.

We are much indebted to the Air Force Photographic Division for copies of aerial photographs of the Bibliando Dome region. For help in the field I wish to thank students who have accompanied me on various occasions, more especially R. C. Sprigg and W. B. Dallwitz. H. E. E. Brock has been responsible for drafting of the aerial photo plot and folding section.

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EXPLANATION OF PLATES.

PLATE X.

Aerial view looking north over portion of the Bibliando Pound in the neighbourhood of Bibliando homestead. The white cross marks the location of Wilyerpa summit.

PLATE XI.

Fig. 1.—Distant view of the accordant summit level of the Wilyerpa ridge as viewed from the north-west.

Fig. 2.—View in vicinity of Wilyerpa summit of the quartzite ridges forming the rim of the Bibliando Pound.

PLATE XII.

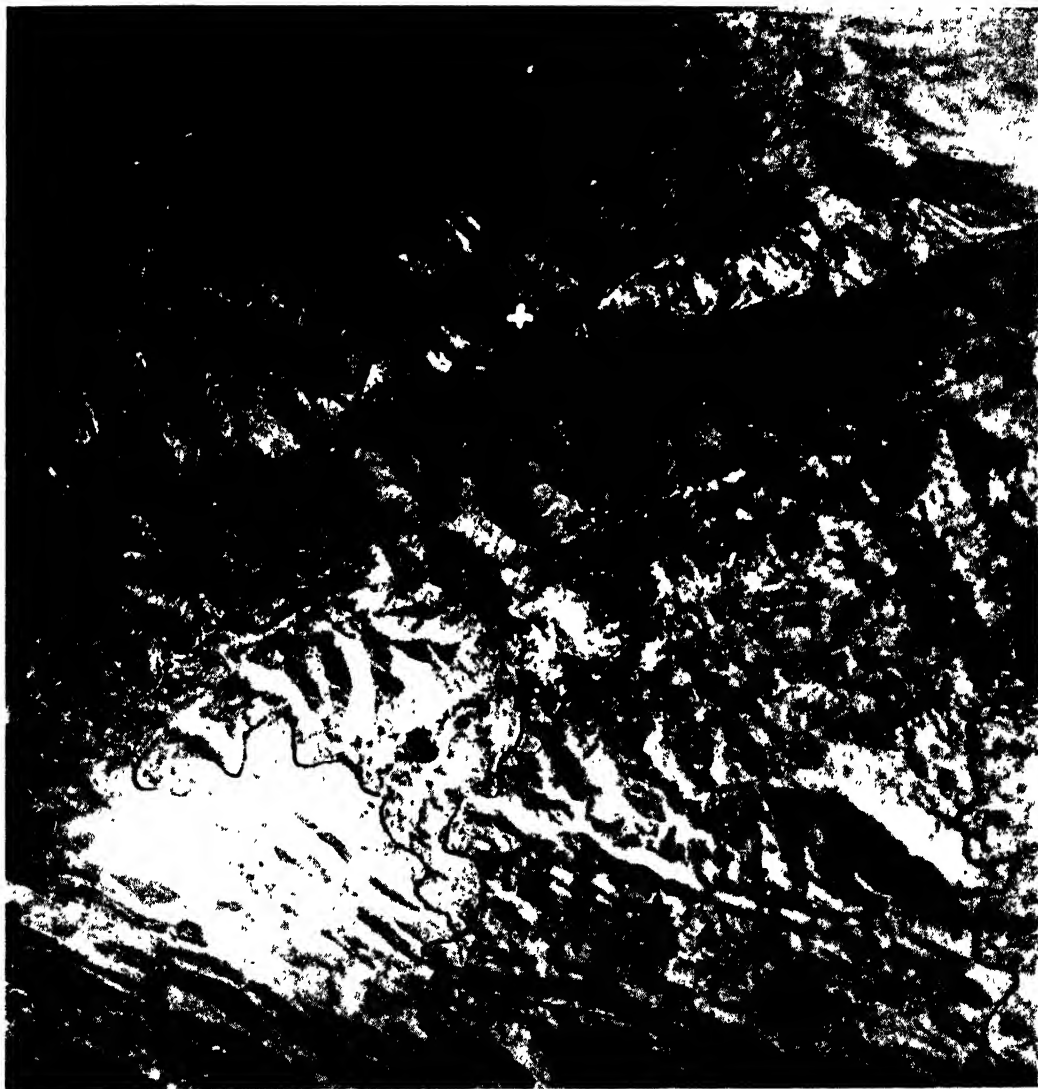
Fig. 1.—Northward dipping strata of the interior of the Pound on the north side.

Fig. 2.—Horizontally disposed strata of the central region of the Pound.

PLATE XIII.

Fig. 1.—Varved glaciogene sediments from the neighbourhood of Glen Warwick.

Fig. 2.—Intraformational, penecontemporaneously crumpled, glaciogene sediments.





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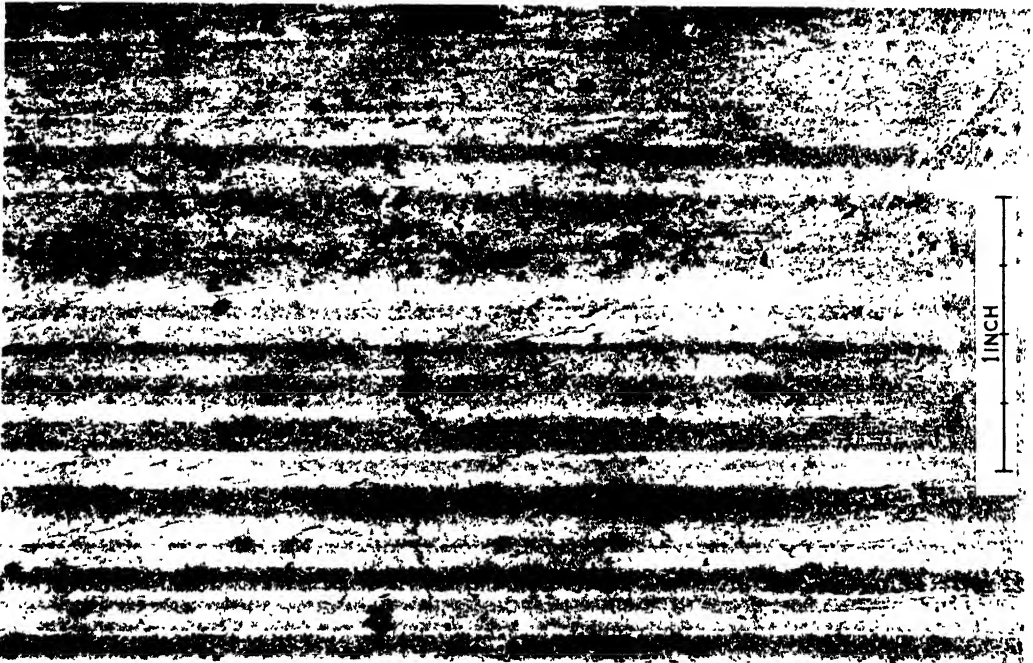
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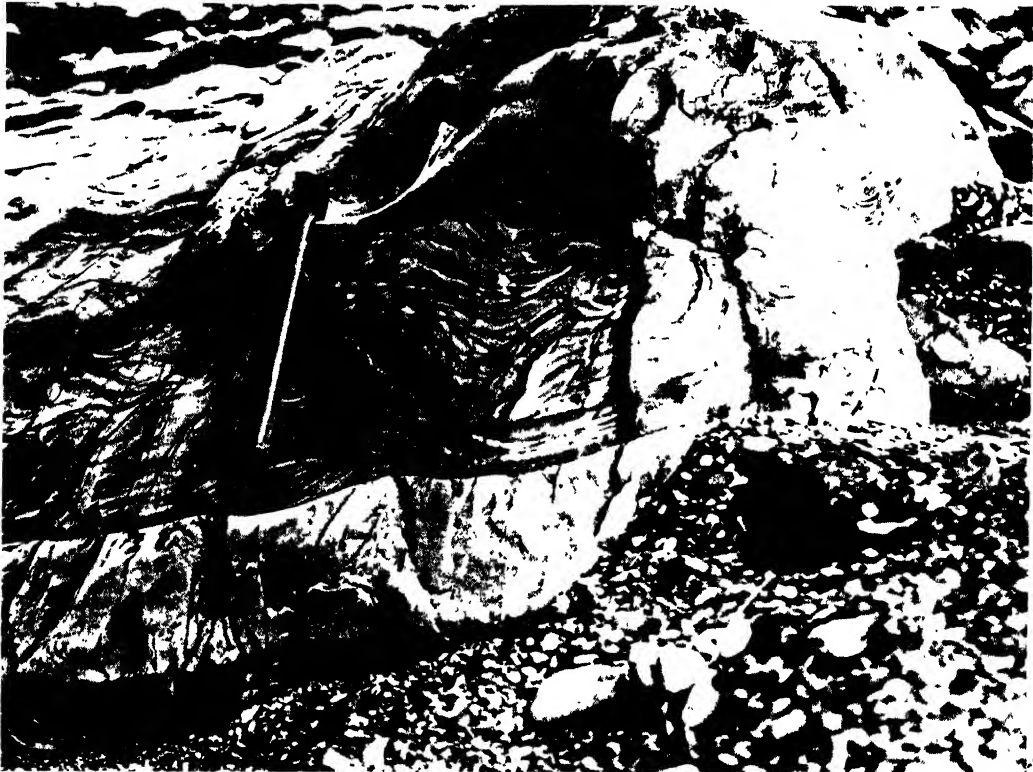
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THE INCOMPLETE NATURE OF THE SYMMETRY RELATIONS BETWEEN THERMODYNAMICAL QUANTITIES.

By R. C. L. BOSWORTH.

Manuscript received, June 20, 1948. Read, August 4, 1948.

Classical chemical thermodynamics is based on the properties of four variables each with the physical dimensions of energy per gramme molecule. These variables, with the symbols as accepted by the Joint Committee, London (1937), are :

- (a) The internal energy : U .
- (b) The free energy : A .
- (c) The enthalpy : H .
- (d) The Gibbs' function or free enthalpy : G .

In a simple single phase system these variables are functions of two pairs of canonically conjugate parameters, namely

The pressure, p , and the molar volume, V ;

The temperature, T , and the molar entropy, S ,
of such a kind that the energy change in any system is

ΔU if the parameters S and V are maintained constant,

ΔA " " " " T " V " " "

ΔH " " " " S " p " " "

ΔG " " " " T " p " " "

The science of thermodynamics owes much of its practical usefulness to the great number of partial differential equations holding between the four variables and the four parameters. Koenig (1935) has shown that these relationships can be classified in groups and Buckley (1944) has described a system of cylindrical tangential contact transformations which can be used in the derivation of all equations in a given group from the prototype. In these transformations U, A, H, G and S, T, p, V enter in a symmetrical manner. However, when we come to consider polycomponent systems the four parameters are insufficient for a complete description of the state of the system and other canonically conjugate pairs must be introduced. The energy of such polycomponent systems obviously depends on the number of molecules of each component present. Let us denote by n_1, n_2 , etc., the mole fractions of the different components or the ratio of the number of molecules of each component to the total number of molecules present. If n_1 is summed over all components, the result is clearly unity. Thus we have

$$\sum_i n_i = 1,$$

so that for a system of m components there are $m-1$ independent parameters n_i . For each n_i we may define a canonically conjugate variable μ_i by

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_j}, \quad (j \neq i) = \left(\frac{\partial U}{\partial n_i} \right)_{V, S, n_j}, \quad (j \neq i) \text{ etc.}$$

μ_i is known as the molar chemical potential for the i th component. For an m component system there are clearly $m-1$ independent μ_i 's.

N.—August 4, 1948.

Neither Koenig nor Buckley made any attempt to absorb the n_1 's and μ_1 's symmetrically into their systems, and with the number of variables limited to four it would clearly be impossible to do so. For ΔA , ΔU , ΔH and ΔG as already defined refer only to changes which occur under conditions of constant n_1 . No variables have been introduced to express the energy changes resulting from a type of reaction in which one or more of the μ_1 's are maintained constant. While it is clearly only a formal matter to introduce such new variables into the body of thermodynamical theory, it would be pointless to do so unless we were first assured that the innovation could be employed in a more elegant treatment of other branches of the subject. To this end it is instructive to consider the interrelations between the different thermodynamical variables and the physical conditions which obtain in industrial chemical operations.

THE DRIVING FORCE FOR CHEMICAL OPERATIONS.

A chemical reaction, considered as a process of transfer from one state to another in a chemical assembly, proceeds under a driving force which, in combination with a resistance coefficient, determines the rate of transfer. The driving force for any chemical reaction is the associated potential energy change. Thus if the physical conditions are maintained isopiestic and adiabatic the driving force will be the enthalpy change ΔH . If the physical conditions are isometric and isothermal, the driving force is the free energy change ΔA . In small scale laboratory work it is generally most convenient to maintain the temperature and pressure constant (as well, of course, as the mole fractions). Accordingly ΔG is the expression most generally used for the driving force in laboratory scale reactions. However, if the same system is to be studied in larger scale equipment, then a simple dimensional argument (Bosworth, 1947a, 1947b) shows that the mechanisms available for removal of the heat of reaction become progressively less and less effective in comparison with the rate of evolution of heat by the reaction. Accordingly a reaction which proceeds effectively under isothermal conditions in small scale equipment will proceed more nearly under adiabatic conditions in very large equipment. In the former case the chemical driving force is ΔG , in the latter it is ΔH . For moderately large equipment where the conditions are neither adiabatic nor isothermal the driving force is intermediate in value between ΔH and ΔG . Weber (1939), for example, has used for such systems a quantity which he calls the availability and denotes by the symbol B . B is defined by $B = H - T_0 S$, whereas $G = H - TS$. Here T is the temperature of the reacting mixture and T_0 that of the sink at which the heat from the reaction is discharged, the temperature of the reaction mixture itself being uncontrolled. As T_0 is made progressively less than T , the difference between B and G is progressively increased.

Let us now suppose that the reaction to be studied in a series of vessels of increasing size were to proceed so rapidly that, in the larger vessels, the volume change produced by the reaction were dissipated at a rate which was slow in comparison with the rate of the reaction. Under such a hypothetical condition the driving force for the reaction, which was ΔG in the smaller vessels, would become ΔA , or the change in the free energy, in the larger vessels. If neither the heat changes nor the volume changes are allowed to dissipate, the driving force becomes ΔU , the change in the internal energy. A given property change will largely be permitted to dissipate if the time taken for the different diffusive mechanisms operative in transporting the property concerned from the reaction point to the walls is small in comparison with the half-life period of a molecule

of a reagent in the reaction zone. Since volume changes are dissipated with the velocity of sound and the time taken for a sound wave to traverse any ordinary sized reaction vessel is small in comparison with the rate constant of any reaction of industrial importance, neither of the two instances mentioned above have, at the moment, any technical significance. However, the rate of removal of heat alone by thermal transport mechanisms in attainable sized reactors is frequently slow in comparison with the reaction rate constant and ΔB or, in extreme cases ΔH , can be taken as the effective chemical driving force.

The removal of the products of reaction from the point at which the reaction occurs can be effected by diffusion, turbulent diffusion or by convection and the rate is frequently slow, often somewhat slower than the transfer of heat. If we neglect for the moment the effect of the reaction heat and consider a system in which p , T and all the n_i 's except n_j are maintained constant, we have a system in which the chemical driving force is not G but $G - n_j \mu_j$. To this quantity which clearly is a new thermodynamical variable we shall give the symbol J_j . There are $m-1$ different quantities of this nature for a system of m components, or if we include among the J_j 's those which refer to energy changes in which one, two or more chemical components are prevented from diffusing to or from the point of reaction there are $(m-1)!$ such variables.

Corresponding to the partial differential equation

$$\left(\frac{\partial J_j}{\partial \mu_i}\right)_{p,T,\mu_1} = -n_j, \quad i \neq j$$

we have the well-known equation

$$\left(\frac{\partial G}{\partial n_j}\right)_{p,T,n_1} = \mu_j, \quad i \neq j.$$

For a binary system there is only one independent n , and therefore only one J . Further, for a binary system forming an ideal solution G is linearly dependent on n and thus J vanishes.

Corresponding to the thermodynamical variables J_j defined above there are others related to the other three ordinary (chemical) thermodynamical variables, viz. :

$$H - n_j \mu_j$$

$$A - n_j \mu_j$$

$$U - n_j \mu_j$$

making in all $4((m-1)!+1)$ variables for a system symmetrical with respect to all chemical parameters. These quantities and the parameters may be represented by a geometrical figure of a considerably higher order of symmetry than the simple two-dimensional one used by Koenig. However, it is only in the case of the two-component system that this figure may be realized in a space of three dimensions.

REPRESENTATION OF THE VARIABLES FOR A TWO-COMPONENT SYSTEM.

In a two-component system there is only one independent n and therefore only one μ . In such a system there are six canonical parameters (T , S , p , V , n , μ) and eight variables (U , A , H , G , $U - n\mu$, $A - n\mu$, $H - n\mu$, $G - n\mu$) which are related to one another in such a way that each variable is a function of three parameters and each parameter is functionally related to four variables. This relationship may thus be represented geometrically either by a cube or by a regular octahedron. The octahedron has eight faces and six corners. Each corner is surrounded by four faces and each face by three corners. Let us inscribe on one particular face a thermodynamical variable (say U) and then proceed to

label the three circumscribing corners with the parameters which are not partial derivatives of the variable; V , S and n if the variable is U . There are two independent ways of labelling these corners, depending on whether V , S or n are arranged clockwise or anti-clockwise around the U face. Having assigned symbols to one face and three corners, there is now only one way of filling in all the other corners and faces. The resultant two representations of the relationships between the thermodynamical quantities are shown in Figure 1. The two forms, it will be seen, are enantiomorphous or are related to one another by a reflective operation. Further, since the octahedra are regular, there are 24 equivalent orientations for each one, or 48 equivalent orientations in all. If any relationship between the thermodynamical quantities is expressed as a relationship between the faces and corners of the octahedron, then up to 47 other equivalent relationships may be obtained by rotation of the two forms of the octahedron. Both Koenig and Buckley were able to show that thermodynamical relationships could be classified in groups, but in their scheme eight was the maximum number of members in any one group. In the present scheme with up to 48 members in a group all useful thermodynamical relationships can be covered by a smaller number of groups.

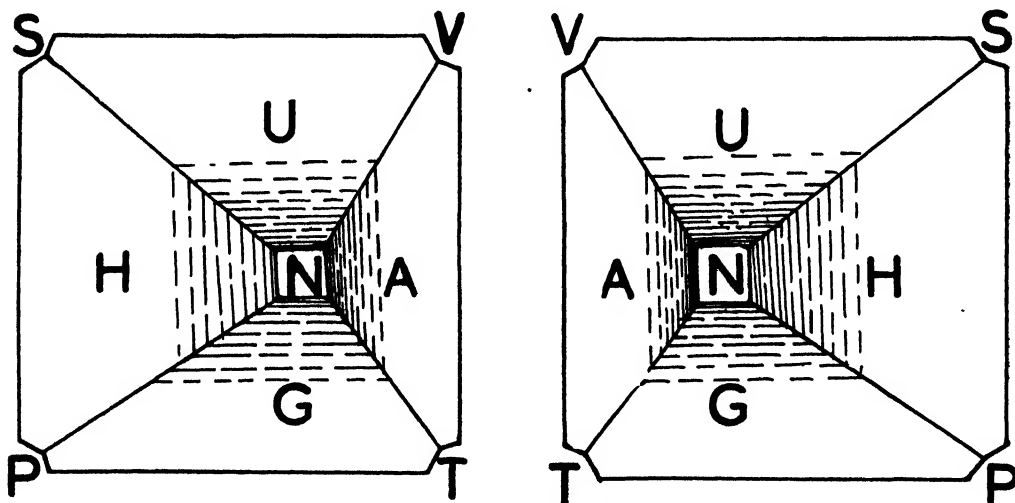


Fig. 1.—The two enantiomorphous octahedra representing the relationship between thermodynamical quantities. The back corner in each case is marked μ , and the back faces $U-n\mu$, $A-n\mu$, $G-n\mu$, $H-n\mu$ to correspond respectively to the U , A , G and H faces shown marked in the diagram.

Before, however, we discuss the grouping of thermodynamical relationships it will be necessary to discuss the question of the algebraic sign of the various quantities. Both Koenig and Buckley have discussed a "rule of signs" to be superimposed on their symmetry schemes in order that the equations derived by rotation or reflection should be correct in this respect. In terms of the new octahedral representation the rule of signs takes a particularly simple form. Three of the parameters (chosen so not to include a conjugate pair) are to be taken as alternatively positive and negative quantities according as they are represented by points of positive or negative co-ordinates in a system of cartesian axes defined by lines through opposite corners of the octahedron. The other three parameters and the variables are always to be taken as positive quantities. The most convenient triad of parameters to select as those which change sign

with orientation are S , p and n , which are all equal to negative partial differential coefficients of the thermodynamical variables, i.e.

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,n}$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{S,n}$$

$$n = -\left(\frac{\partial J}{\partial \mu}\right)_{T,p}.$$

EQUIVALENT THERMODYNAMICAL REPRESENTATIONS.

The various orientations of the different octahedral faces and corners may be described by a scheme which labels the three positive corners x , y , z , the three negative corners, \bar{x} , \bar{y} , \bar{z} , the four front faces a , b , c , d and the four back faces \bar{a} , \bar{b} , \bar{c} , \bar{d} . Let us take as the standard orientation the one for which

$x = S$	$\bar{x} = T$
$y = V$	$\bar{y} = -p$
$z = n$	$\bar{z} = \mu$
$a = U$	$\bar{a} = U - n\mu$
$b = H$	$\bar{b} = H - n\mu$
$c = G$	$\bar{c} = G - n\mu$
$d = A$	$\bar{d} = A - n\mu$

Then when the octahedron is subject to the 48 possible rotations and reflections 47 other equivalent representations will be reproduced. These equivalent representations are given in Table 1. Since $U - n\mu$, etc., never occur directly in the standard forms for thermodynamical equations, the \bar{a} , \bar{b} , \bar{c} , \bar{d} faces will not be given in the table. The representations referred to as $S_{(\text{subscript})}$ are obtained by rotations of the standard representation referred to as S_1 . The representations marked $R_{(\text{subscript})}$ are obtained by reflections of $S_{(\text{subscript})}$.

THERMODYNAMICAL RELATIONSHIPS.

The representation of thermodynamical relationships as members of a limited number of groups is illustrated in Table 2. Here all the ordinary zero and first order relationships are covered in seven groups. Each group may be represented by a symbolic equation in x , y , z , \bar{x} , \bar{y} , \bar{z} , a , b , c and d , and by operating on this equation with the various operators from S_1 to R_{24} all the various members of the group may be formed. The number of members of the group obviously depends on the degree of symmetry of the symbolic equation and may be 48 or any proper fraction of 48.

Further, the members of these groups are not all independent. Thus S_{10} operating on group IV gives

$$\left(\frac{\partial U}{\partial \mu}\right)_{V,S} = \mu \left(\frac{\partial n}{\partial \mu}\right)_{V,S}$$

and an identical equation is obtained by the operation of S_{10} on group III. Further, operation of S_{22} on both groups III and IV gives a single expression, namely

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T}$$

and there occurs several similar cases of overlapping between the groups.

TABLE 1.

Operation.	Positive Corners.			Negative Corners.			Front Faces.			
Type.	x	y	z	\bar{x}	\bar{y}	\bar{z}	a	b	c	d
S_1	S	V	n	T	-p	μ	U	H	G	A
R_1	S	V	μ	T	-p	-n	U-n μ	H-n μ	G-n μ	A-n μ
S_2	p	S	n	V	T	μ	H	G	A	U
R_2	p	S	μ	V	T	-n	H-n μ	G-n μ	A-n μ	U-n μ
S_3	T	p	n	-S	V	μ	G	A	U	H
R_3	T	p	μ	-S	V	-n	G-n μ	A-n μ	U-n μ	H-n μ
S_4	V	T	n	-p	-S	μ	A	U	G	G
R_4	V	T	μ	-p	-S	-n	A-n μ	U-n μ	H-n μ	G-n μ
S_5	S	p	μ	T	V	-n	H-n μ	U-n μ	A-n μ	G-n μ
R_5	S	p	n	T	V	μ	H	U	A	G
S_6	V	S	μ	-p	T	-n	U-n μ	A-n μ	G-n μ	H-n μ
R_6	V	S	n	-p	T	μ	U	A	G	H
S_7	T	V	μ	-S	-p	-n	A-n μ	G-n μ	H-n μ	U-n μ
R_7	T	V	n	-S	-p	μ	A	G	H	U
S_8	p	T	μ	V	-S	-n	G-n μ	H-n μ	U-n μ	A-n μ
R_8	p	T	n	V	-S	μ	G	H	U	A
S_9	S	μ	V	T	-n	-p	U-n μ	U	A	A-n μ
R_9	S	μ	p	T	-n	V	H-n μ	H	G	G-n μ
S_{10}	n	S	V	μ	T	-p	U	A	A-n μ	U-n μ
R_{10}	n	S	p	μ	T	V	H	G	G-n μ	H-n μ
S_{11}	T	n	p	-S	μ	-p	A	A-n μ	U-n μ	U
R_{11}	T	n	p	-S	μ	V	G	G-n μ	H-n μ	H
S_{12}	μ	T	p	-n	-S	-p	A-n μ	U-n μ	U	A
R_{12}	μ	T	p	-n	-S	V	G-n μ	H-n μ	H	G
S_{13}	S	n	p	T	μ	V	H	H-n μ	G-n μ	G
R_{13}	S	n	p	T	μ	-p	U	U-n μ	A-n μ	A
S_{14}	μ	S	p	-n	T	V	H-n μ	G-n μ	G	H
R_{14}	μ	S	p	-n	T	-p	U-n μ	A-n μ	A	U
S_{15}	T	μ	p	-S	-n	V	G-n μ	G	H	H-n μ
R_{15}	T	μ	p	-S	-n	-p	A-n μ	A	U	U-n μ
S_{16}	n	T	p	μ	-S	V	G	H	H-n μ	G-n μ
R_{16}	n	T	p	μ	-S	-p	A	U	U-n μ	A-n μ
S_{17}	p	μ	S	V	-n	T	H-n μ	H	U	U-n μ
R_{17}	p	μ	T	V	-n	-S	G-n μ	G	A	A-n μ
S_{18}	n	p	S	μ	V	T	H	U	U-n μ	H-n μ
R_{18}	n	p	T	μ	V	-S	G	A	A-n μ	G-n μ
S_{19}	V	n	S	-p	μ	T	U	U-n μ	H-n μ	H
R_{19}	V	n	T	-p	μ	-S	A	A-n μ	G-n μ	G
S_{20}	μ	V	S	-n	-p	T	U-n μ	H-n μ	H	U
R_{20}	μ	V	T	-n	-p	-S	A-n μ	G-n μ	G	A
S_{21}	p	n	T	V	μ	-S	G	G-n μ	A-n μ	A
R_{21}	p	n	T	V	μ	T	H	H-n μ	U-n μ	U
S_{22}	μ	p	T	-n	V	-S	G-n μ	A-n μ	A	G
R_{22}	μ	p	T	-n	V	T	H-n μ	U-n μ	U	H
S_{23}	V	μ	S	-p	-n	-S	A-n μ	A	G	G-n μ
R_{23}	V	μ	S	-p	-n	T	U-n μ	U	H	H-n μ
S_{24}	n	V	T	μ	-p	-S	A	G	G-n μ	A-n μ
R_{24}	n	V	S	μ	-p	T	U	H	H-n μ	U-n μ

This limited overlapping arises from the fact that we have not adopted separate names and symbols for the quantities $G-n\mu$, $H-n\mu$, $U-n\mu$ and $A-n\mu$ which in the scheme outlined above have as much right to be considered as thermodynamical variables as G , H , U and A . A further overlapping of the groups in Table 2 would result if, say, G were replaced by $A+pV$ or $H-TS$. It would seem desirable, therefore, to allocate new symbols to the four variables above, and the following are suggested:

$$\begin{aligned} J &= G - n\mu \text{ (as above)} \\ I &= H - n\mu \\ W &= U - n\mu \\ Z &= A - n\mu. \end{aligned}$$

Use of these quantities besides eliminating overlapping in Table 2 would also increase the membership of some of the smaller groups.

TABLE 2.
Grouped Thermodynamical Relationships.

Type.	Group Equation.	Typical Members.	No. in Group.
I	$da = \bar{x}dx + \bar{y}dy + \bar{z}dz$	$dU = TdS - pdV + \mu dn$	4
II	$a = c + \bar{x}\bar{x} + \bar{y}\bar{y}$	$\begin{cases} G = U - TS + pv \\ U = A + TS \end{cases}$	6
III	$x = -\left(\frac{\partial d}{\partial \bar{x}}\right)_{\bar{y}, \bar{z}}$	$S = -\left(\frac{\partial A}{\partial T}\right)_{v, n}$	24
IV	$a = d - \bar{x}\left(\frac{\partial d}{\partial \bar{x}}\right)_{\bar{y}, \bar{z}}$	$U = A - T\left(\frac{\partial A}{\partial T}\right)_{v, n}$ (Gibbs-Helmholtz Equation)	24
V	$\left(\frac{\partial \bar{y}}{\partial \bar{x}}\right)_{\bar{y}, \bar{z}} = -\left(\frac{\partial \bar{x}}{\partial \bar{y}}\right)_{\bar{x}, \bar{z}}$	$\left(\frac{\partial p}{\partial T}\right)_{v, n} = \left(\frac{\partial S}{\partial V}\right)_{T, n}$	24
VI	$\left(\frac{\partial \bar{x}}{\partial \bar{y}}\right)_{\bar{y}, \bar{z}} = -\left(\frac{\partial \bar{x}}{\partial \bar{y}}\right)_{\bar{x}, \bar{z}}\left(\frac{\partial \bar{y}}{\partial \bar{x}}\right)_{\bar{x}, \bar{z}}$	$\left(\frac{\partial S}{\partial T}\right)_{p, n} = -\left(\frac{\partial S}{\partial p}\right)_{T, n}\left(\frac{\partial p}{\partial T}\right)_{S, n}$	24
VII	$\left(\frac{\partial a}{\partial \bar{y}}\right)_{\bar{x}, \bar{z}} = -\bar{x}\left(\frac{\partial \bar{y}}{\partial \bar{x}}\right)_{\bar{y}, \bar{z}} + \bar{y}$	$\left(\frac{\partial U}{\partial V}\right)_{T, n} = T\left(\frac{\partial p}{\partial T}\right)_{v, n} - p$	48

REPRESENTATION OF THE CHANGE FROM SMALL TO LARGE SCALE CONDITIONS.

As has been indicated earlier in this paper, the limited rates for the diffusion of matter and heat which obtain in all reaction vessels means that a reaction which takes place under effective conditions of constant T and n when studied on the small scale will take place under conditions of constant S and μ when studied on a very large scale. This means that any thermodynamical relationship represented by the operator R_{11} of Table 1 for small scale operation will become replaced by the operator R_0 for very large scale operation. The change of R_{11} to R_0 is a change from the representation

$T, n, p, -S, \mu, V, G, J, I, H$, to

$S, \mu, p, T, -n, V, I, H, G, J$.

with a change in the effective driving force from ΔG to ΔI or to $\Delta G + T\Delta S - \mu\Delta n$.

SUMMARY.

The schemes for the representation of the symmetry relations between the thermodynamical variables and parameters proposed by Koenig and by Buckley do not include the chemical variables n_1 and μ_1 in a symmetrical manner. A representation with a considerably higher degree of symmetry may be obtained by the introduction of four new thermodynamical variables: $J=G-n\mu$, $I=H-n\mu$, $Z=A-n\mu$ and $W=U-n\mu$. The eight variables are then represented by the eight faces of a regular octahedron and the six parameters p , T , V , S , n and μ by the six corners. These are arranged in such a way that the variable represented on any one face is a function of the three parameters on the circumscribing three corners; and each corner is surrounded by the four faces whose variables are functionally related to the parameter represented by the corner. There are two enantiomorphous forms of the octahedron which will satisfy these conditions and rotation of either will give in all 48 equivalent representations of the thermodynamical properties and the various relationships between these properties may be reduced to a small number of groups each containing either 48 or a proper fraction of 48 members.

Consideration is given to the change in the thermodynamical conditions which obtains when the size of the equipment in which a given reaction is studied is increased without limit. Conditions of constant T , n and p for small scale equipment become conditions of constant S , μ and p in very large scale equipment on account of the relative slowness of the diffusion of matter and heat in the reacting mixture. This change is equivalent to a rotary operation on the octahedron representing the thermodynamical properties.

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SOME RECENT WORK ON THE SEPARATION AND USE OF STABLE ISOTOPES.*

By I. LAUDER.

Mr. President, Ladies and Gentlemen,

I wish to express my appreciation of the invitation to deliver this year's Liversidge Research Lecture as this is, indeed, a high honour. The University of Queensland is greatly handicapped by its isolation, and it is not often that a member of its staff is asked to deliver a special lecture at some other university. For this reason, too, I very much appreciate the invitation.

I have chosen for the title of this address "Some Recent Work on the Separation and Use of Stable Isotopes". There have been many outstanding achievements in science in the past ten to fifteen years, and I think that the development of methods for separating isotopes must come within this category, not only because of its immediate interest to chemistry, but also because a vast amount of important information has been gained by the use of the separated isotopes.

The existence of isotopes of radio-active elements was first established in 1911, and two years later J. J. Thomson demonstrated for the first time the existence of isotopes of a stable element—neon—of mass numbers 20 and 22. With the subsequent development of the mass-spectrograph by Aston, the isotopic compositions of most elements are now known.

Although the basic principles of most of the methods now used for the separation of isotopes have been known for many years, it was not until 1932 and later that any large-scale separations were achieved. It is interesting to note that work on the detection and separation of isotopes was suspended during World War I, whereas during World War II such work reached an immense climax with the development of the atomic bomb.

PART I. METHODS OF SEPARATION.

Except in the case of hydrogen, only small differences in chemical and physical properties of isotopes exist, and these differences decrease relatively with increasing atomic weight, thus increasing the difficulty of separation. The hydrogen isotopes were the first to be separated in an almost pure state. This was achieved in 1933 by Lewis and MacDonald⁽¹⁾ by the continued electrolysis of water. The process is so well known that it need not be considered further, but it may be added that in the case of isotopes of other elements only very small separations have been obtained by electrolysis.

The separation of small amounts of ions of different masses has been achieved by the use of the mass-spectrograph and, during the war years, a large-scale development of this method took place for the separation of the uranium isotopes. I am not familiar with this development and may be permitted to exclude it from further consideration.

Omitting, then, any discussion on the electrolytic and the electromagnetic methods, the following methods have been used to achieve considerable degrees

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of separation: (1) diffusion, (2) distillation, (3) chemical exchange, (4) thermal diffusion. The important applications of each of these methods will be considered and, in addition, the centrifugal method of separation may be considered. This latter method has not resulted in any important degree of separation as yet, but it may become of importance in the future, especially for the separation of isotopes of high molecular weight.

(1) *Diffusion Methods.*

The rate of gaseous diffusion varies inversely as the square root of the molecular weight, and so isotopic molecules should diffuse at slightly different rates. This method was first applied by Aston in an attempt to separate the isotopes of neon, but only a very limited success was achieved. The atomic weight of neon of normal isotopic ratio is 20.2, while Aston obtained ultimately two fractions with atomic weights 20.15 and 20.28 respectively.

In all methods of separation a quantity known as the separation factor is of interest. This is given by the ratio of the isotopes after applying the separation process to the ratio before applying the separation process. That is, the separation factor with respect to the heavy molecules,

$$S = \frac{N_h/N_l \text{ (after applying separation process)}}{N_h/N_l \text{ (before applying separation process)}}$$

where N_h , N_l stand for the numbers of heavy and light molecules respectively. To achieve a maximum separation by the diffusion method, it is necessary to ensure that there is perfect mixing of the gas on each side of the porous barrier through which diffusion occurs and also that the mean pore diameter of the barrier is small in comparison with the mean free path of the diffusing gas. This is a rather stringent condition, as for most gases at one atmosphere pressure and room temperature the mean free path is of the order 10^{-5} cm. The mean free path varies inversely with pressure, and so by working at lower pressures a barrier with a larger pore diameter may be used.

For a separation by gaseous diffusion under ideal conditions the separation factor (with respect to the heavy molecules) is given approximately by the expression

$$S = \frac{M_2 + M_1}{M_2 - M_1} \sqrt{\frac{\text{Initial Volume}}{\text{Final Volume}}} \dots\dots\dots (2)$$

where M_2 and M_1 stand for the molecular weights of the heavy and light molecules respectively. If half of the initial volume of gas is allowed to diffuse through the barrier, then, for the neon isotopes of molecular weights 22 and 20, $S=1.034$. Thus only a small degree of separation is achieved in each diffusion unit, but by connecting a sufficient number of units in series any desired concentration of isotope may be achieved. The over-all separation factor for n units in series equals S^n .

The first successful apparatus for the continuous separation of isotopes by gaseous diffusion at low pressure was devised by Hertz⁽²⁾ in 1932, using porous porcelain tubes as the diffusion barrier. With 48 units operating in series, Hertz⁽³⁾ produced practically pure ^{22}Ne from normal neon. In the same apparatus, starting from hydrogen containing 10% deuterium, spectroscopically pure deuterium⁽⁴⁾ was isolated. Carbon⁽⁵⁾ containing 16% ^{13}C and nitrogen⁽⁶⁾ containing 3% ^{15}N have been isolated by this type of diffusion method.

Later, in 1934, Hertz⁽⁷⁾ produced a still more efficient unit in which a stream of mercury vapour served as the diffusion barrier, and at the same time it served to pump the gas undergoing diffusion from one unit to another. This modification has been used to produce oxygen⁽⁷⁾ containing 0.5% ^{18}O , argon⁽⁸⁾ containing 50% ^{36}Ar , carbon⁽⁹⁾ containing 30% ^{13}C , and nitrogen⁽¹⁰⁾ containing 9% ^{15}N .

Any account of the diffusion method of separation of isotopes could not be regarded as complete without some mention of its recent application to the separation of the uranium isotopes ^{235}U and ^{238}U using uranium hexafluoride, UF_6 , as the carrier gas. A limited amount of information on the process is given in the Smythe Report.⁽¹¹⁾ Assuming that the separation factor for a single unit is 1.0013 and that 4,000 units are operated in series, the over-all separation factor comes out to 173.8. If the first unit is fed with UF_6 of normal isotopic ratio (0.7% $^{235}\text{UF}_6$), UF_6 containing approximately 55.5% $^{235}\text{UF}_6$ would be produced in the last unit when equilibrium is established. The concentrating cascade of 4,000 units would be run in combination with a stripping cascade for treating the impoverished gas from stage 1. By a partial removal of $^{238}\text{UF}_6$ in the stripping cascade, the $^{235}\text{UF}_6$ content of the impoverished gas is built up to its normal value. The gas from the first unit of the stripping cascade is then recirculated to the first unit of the concentrating cascade. If it is economical to discard the UF_6 when the $^{235}\text{UF}_6$ content has been reduced to half the normal value, the stripping cascade would consist of about 538 units operating in series.

For each cubic centimetre of 55.5% $^{235}\text{UF}_6$ withdrawn from the last unit of the concentrating cascade 157 c.c. of 0.35% $^{235}\text{UF}_6$ would be drawn off from the last unit of the stripping cascade. These withdrawals would be balanced by the input of 158 c.c. of normal UF_6 to stage 1. For each cubic centimetre of output from the last unit of the concentrating cascade about 120 litres of UF_6 would pass through the first unit, and so the total circulation in all stages would be very high indeed.

(2) Distillation.

The separation of liquids of different boiling points by fractional distillation is a well-understood process. Experiment shows that a fractionation column of the packed type gives concentrations in accordance with the formula

$$\frac{C_t}{1-C_t} \bigg/ \frac{C_b}{1-C_b} = \alpha^K \quad \dots\dots\dots (3)$$

where C_t and C_b are the mole fractions of one constituent at the top and bottom respectively. α is the ratio of the vapour pressures and K is the number of theoretical plates. Values of α for H_2^{16}O and H_2^{18}O forms of water at various temperatures are given in the following table.⁽¹²⁾

TABLE 1.

Temperature °C.	α
11.25	1.013
35.6	1.008
46.35	1.007
100.0	1.003

When α is nearly unity, as it is in the case of the separation of most isotopes, K must be large if a large change in the concentration of isotopes is desired. To secure a large K , the length of the column should be made large, and also the efficiency of the column should be made as high as possible by the use of a suitable packing material. The value of α increases with decreasing temperature and so the degree of separation is increased by working at as low a temperature as is conveniently possible.

The method has found its chief application to the separation of the isotopic forms of water. In one column six inches in diameter and 35 feet high set up by Pegram, Huffmann, and Urey,⁽¹³⁾ after 300 hours operation water containing 0.85% ^{18}O was produced. If equilibrium had been set up, approximately 20 c.c. of water containing about 2.5% ^{18}O could have been withdrawn daily. In the same still Roberts and Urey⁽¹⁴⁾ fractionated normal methyl alcohol to produce alcohol enriched in the heavy oxygen isotope ^{18}O . No separation of the heavy carbon forms of the alcohol was obtained.

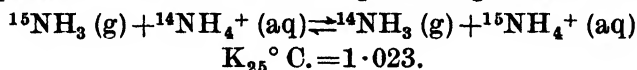
The vapour pressures of the isotopic hydrogen forms of water differ more than the vapour pressures of the isotopic oxygen forms of water.⁽¹²⁾ Accordingly, it is found that deuterium concentrates at a faster rate than the heavy oxygen during the fractionation process. The Smythe Report mentions that one of the methods used for the separation of deuterium required for the work on atomic energy was by the fractionation of water, but no details of the still used are given.

Recently, Dostrovsky and Hughes⁽¹⁵⁾ have published a short note giving details of a very efficient packed column 0.8 inch internal diameter and 12 feet high which produced after 24 hours' operation 500 c.c. of water containing 0.2% D and 0.55% ^{18}O . It is apparent from these figures that the column is highly efficient and is capable of supplying relatively large quantities of the heavy isotopes of hydrogen and oxygen at concentrations usually sufficient for exchange experiments.

(3) *Chemical Exchange.*

If the chemical properties of isotopes were identical, the equilibrium constants for isotopic exchange reactions would be unity. That this is not so was first indicated by the calculation of equilibrium constants of certain exchange reactions by Urey and Rittenberg.⁽¹⁶⁾ For reactions involving isotopes of elements of low atomic weight, the constants usually differ from unity by a few per cent., but this difference decreases with increasing atomic weight and also with increasing temperature. The chemical method of separating isotopes is thus restricted to isotopes of low atomic weight and it is best carried out at as low a temperature as is conveniently possible.

For the separation of ^{15}N the following exchange reaction was used :

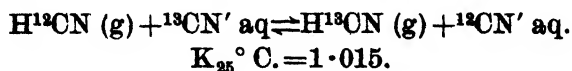


The ^{15}N collects preferentially in the liquid phase.

The technique of the method is to establish a counter-current flow of ammonium nitrate solution and ammonia gas in a packed fractionating column. If several columns are operated in series, the sizes are reduced proportionally so as to keep the transport of the heavy isotope in each column practically the same. If the first column increases the concentration of ^{15}N by a factor of 10, for example, 9/10 of the liquid draining out of the bottom of the column is mixed with sodium hydroxide solution. The ammonia liberated is fed back into the bottom of the first column together with the ammonia issuing from the top of the second column. The remaining 1/10 of the flow from column 1 is fed into the top of the second column, and so on.

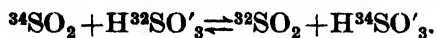
Using a three-stage apparatus of total length 43.5 metres, Urey⁽¹⁷⁾ and co-workers isolated nitrogen containing 70.6% ^{15}N .

Heavy carbon, ^{13}C , has been concentrated by making use of the exchange reaction⁽¹⁸⁾



The ^{13}C tends to collect in the gas phase. In a two stage apparatus up to 22% ^{13}C has been produced at the rate of 0.1 gm. ^{13}C per day.

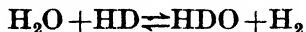
For the concentration of ^{34}S use was made of the exchange reaction⁽¹⁹⁾



$$K_{25}^\circ \text{C.} = 1.012.$$

In a three-stage apparatus sulphur containing 25% ^{34}S was produced at the rate of 3.2 gm. per day.

As mentioned in the Smythe Report, the exchange reaction between water vapour and gaseous hydrogen in the presence of a suitable catalyst was used during the atomic bomb work for concentrating heavy hydrogen. The equilibrium favours the accumulation of deuterium in the water.⁽²⁰⁾



$$K_{25}^\circ \text{C.} = 2.67; \quad K_{100}^\circ \text{C.} = 2.00.$$

(4) Thermal Diffusion.

In 1938 Clusius and Dickel⁽²¹⁾ introduced a method of separation of isotopes by thermal diffusion which has proved very effective in many cases. Essentially, the apparatus consists of a vertical water-jacketed tube down the centre of which is stretched a wire which may be heated electrically to the desired temperature. The partial separation of light and heavy molecules which this type of apparatus may produce in a gaseous mixture is due to two effects: (1) due to thermal diffusion, the heavy molecules tend to concentrate near the cool wall of the tube and the light molecules near the hot wire; (2) due to the difference in density between the cold gas and the hot gas, a thermal siphon is set up in the tube which transports the light molecules to the top of the tube and the heavy molecules to the bottom of the tube. The separation produced by these two effects increases until it is just counterbalanced by the remixing effect of ordinary diffusion.

The various factors which influence the efficiency of such separation columns have been investigated by many workers.⁽²²⁾ For a gas containing molecules of weights M_1 and M_2 and mol. fractions C_1 and C_2 respectively, subjected to a thermal gradient (in the absence of convection currents), the relative difference in mol. fraction of either constituent is given by

$$\Delta C = k_T \log_e T_2/T_1 \dots\dots\dots (5)$$

where T_2 and T_1 ($T_2 > T_1$) represent the temperatures at the two ends of the gradient and k_T is the coefficient of thermal diffusion. For isotopic molecules behaving as elastic spheres,

$$k_T = \frac{105}{118} \times \frac{M_2 - M_1}{M_2 + M_1} \times C_1 C_2 \dots\dots\dots (6)$$

Due to deviations from the perfect gas state, the k_T values for real gases are found to be less than the calculated values. Approximate values of k_T for actual gases may be obtained from viscosity data.⁽²³⁾ If S is the repulsive force index of the molecules and η the coefficient of viscosity, then

$$k_T (\text{actual gas}) = k_T (\text{perfect gas}) \times \frac{S-5}{S-1} \dots\dots\dots (7)$$

and

$$\log \eta = \frac{S+3}{2(S-1)} \log T + \text{constant} \dots\dots\dots (8)$$

If $S > 5$, the heavy molecules tend to concentrate near the cold end of the gradient; if $S < 5$, the separation occurs in the opposite direction; if $S = 5$, no separation by thermal diffusion is possible. Some values for $(S-5)/(S-1)$ for various gases are given in Table 2.

This data suggests that carbon monoxide would prove more suitable than oxygen for the separation of the oxygen isotopes, but other factors such as ease of preparation in a pure state and thermal stability must be considered.

The concentration of heavy isotope at the bottom of a separation tube when equilibrium is set up is found to be proportional to (1) r^{-4} , where r is the radius of the tube, (2) the length of the tube provided the mol. fraction is within the range 0.25–0.75, (3) p^{-2} provided the pressure is not too low.

The rate at which equilibrium is established in a column is proportional to r^4 and to p^2 . In practice, it is found that the time required to establish a given concentration difference may be decreased by starting the apparatus at a pressure greater than the optimum working pressure and subsequently as the separation proceeds by reducing the pressure to the optimum working pressure.⁽²⁴⁾

The separation of the chlorine isotopes ^{35}Cl and ^{37}Cl in an almost pure state using HCl as the carrier was achieved by Clusius and Dickel in 1939, using a five-stage apparatus of total length 36 metres and a wire temperature 690°C . The diameter of one tube was 12.8 mm., while all the other tubes had the same diameter, namely 8.4 mm. After 17 days' continuous operation, 8 c.c. H^{37}Cl and 25 c.c. H^{35}Cl could be withdrawn per day. The ^{35}Cl was 99.6% pure and the ^{37}Cl 99.4% pure.

TABLE 2.

Gas.	S.	$\frac{S-5}{S-1}$
He	13.1	0.67
Cl_2	5.1	0.02
O_2	9.7	0.54
CO	11.8	0.63
SO_2	4.6	-0.10

The separation of the chlorine isotopes represents a particularly favourable case, as normal chlorine contains 76% ^{35}Cl and 24% ^{37}Cl . The separation of isotopes of low abundance presents a more difficult problem.

In addition to the separation of the chlorine isotopes, Clusius and Dickel have separated the following isotopes in an almost pure form: ^{20}Ne and ^{22}Ne ⁽²⁶⁾; ^{84}Kr and ^{86}Kr ⁽²⁷⁾; $^{18}\text{O}_2$.⁽²⁸⁾ In an attempt to separate heavy nitrogen, Clusius and Dickel⁽²⁸⁾ obtained almost pure ^{14}N . ^{15}N . The equilibrium $2^{14}\text{N} \cdot ^{15}\text{N} \rightleftharpoons ^{14}\text{N}_2 + ^{15}\text{N}_2$ was not established at the temperature of the wire in the separation tube. Partial separations⁽²⁹⁾ of isotopes of carbon, nitrogen and hydrogen have also been reported.

Recently, a considerable degree of separation of the heavy isotopes of carbon and of oxygen was achieved by Taylor and Bernstein⁽³⁰⁾ by a combination of a chemical exchange process and thermal diffusion in a mixture of CO_2 and CO .

Bramley and Brewer⁽³¹⁾ introduced a slight modification of the Clusius and Dickel apparatus by using two concentric tubes, the inner one being heated and the outer one cooled. A greater volume of gas may be treated by this apparatus but it is not so easy to maintain the high temperature gradient as is generally used in the Clusius and Dickel apparatus.

(5) Centrifugation.

The possibility of separating isotopes by a centrifugal method has been considered from time to time, but little advance had been made until the introduction of the Beams⁽³²⁾ air-driven centrifuge.

The separation factor as already defined is given by the equation

$$S = \exp \frac{(M_2 - M_1)v^2}{2RT} \dots\dots\dots (4)$$

where v is the peripheral velocity and M_2 and M_1 are the molecular weights of the constituents of the gas. It will be noticed that S depends on the difference of the masses of the two isotopes and for a given value of $M_2 - M_1$ the method should be just as effective for the separation of isotopes of high molecular weight as for isotopes of low molecular weight.

For the uranium isotopes ^{235}U and ^{238}U , $M_2 - M_1 = 3$, and with $v = 5 \times 10^4$ cm./sec. and $T = 300^\circ \text{K.}$, $S = 1.16$ as compared with the value $S = 1.0013$ for a single stage of the diffusion method already considered. Under the above conditions the separation produced by one centrifugation would equal the separation produced by 115 diffusion units operating in series. A pilot centrifugal plant for the separation of the uranium isotopes was put into operation during the war years, but no large-scale plant was set up.

To achieve large separations a cascade system of centrifuges would be required and it is possible that future development will be along these lines.

The results achieved by the application of the various methods of separation are listed in Table 3.

TABLE 3.
Separations Achieved.

Method.	Isotope.	Normal Abundance of Isotope in Per Cent.	Degree of Separation in Per Cent.	Date Achieved.
Electrolysis	^2H	0.02	~ 100	1933
Diffusion	^2H	0.02	$\sim 100^*$	1933
"	^{23}Ne	9.73	~ 100	1934
"	^{18}O	0.2	0.5	1934
"	^{36}A	0.307	50	1937
"	^{13}C	1.1	30	1938
"	^{15}N	0.38	9	1938
Distillation	^{18}O	0.2	0.85	1937
Chemical exchange	^{15}N	0.38	70.6	1939
"	^{13}C	1.1	22	1940
"	^{34}S	4.2	25	1940
Thermal diffusion	^{37}Cl	24	99.4	1939
"	^{35}Cl	76	99.6	1939
"	^{20}Ne	90	~ 100	1940
"	^{22}Ne	9.73	~ 100	1940
"	^{86}Kr	57.10	~ 100	1943
"	^{86}Kr	17.47	~ 100	1943
"	^{18}O	0.2	~ 100	1943
"	^{15}N	0.38	~ 50	1943

* This separation was achieved by using hydrogen containing 10% deuterium as the starting material.

PART II. USES OF ISOTOPES.

In recent years, both stable and radio-active isotopes of many elements have found extensive application to the study of problems in physics, chemistry and biology. If a suitable radio-active isotope of the element in question is available it is perhaps easier to use as a tracer than a stable isotope. However,

in the cases of hydrogen, oxygen, nitrogen and carbon the stable isotopes have so far proved of greater value than the corresponding radio-active isotopes.

The fundamental principle underlying the use of any isotopic tracer element is that the tracer behaves in any reaction in exactly the same way as the normal element. This is true within the usual limits of experimental error provided the concentration of the isotopic tracer is not too great.

The general chemistry of the exchange reactions of heavy hydrogen is well known, and in the remaining discussion we shall consider chiefly applications of the isotopes of oxygen, nitrogen and carbon.

It is not my intention to deal with the biological applications of the separated stable isotopes other than by giving one brief example of the use of heavy hydrogen to study fat-metabolism in rats and mice. In principle, the technique used is as follows: The mice are fed with a fat or fatty-acid labelled with a few per cent. of deuterium and, after a suitable period, the animals are killed. The fatty acids are then isolated and burnt in oxygen. The water formed is collected and, after purification, its isotopic composition is determined usually by a density method.

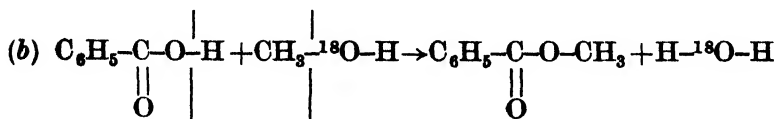
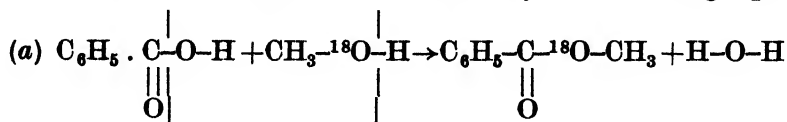
The deuterium-labelled fatty acid is readily prepared. When a fatty acid is heated with D_2SO_4 an exchange of H for D occurs only at the α -carbon atom. On the other hand, when a fatty acid is heated with D_2O at $130-135^\circ C.$ in the presence of alkali and an active platinum catalyst exchange occurs for all hydrogen atoms on the carbon chain.⁽³³⁾

In one experiment Stetten and Schoenheimer⁽³⁴⁾ fed the ethyl ester of deuterium-labelled palmitic acid to rats and, subsequently, isolated palmitic, stearic, myristic, lauric, palmitoleic and oleic acids, all containing more deuterium than normal, showing that these acids had been formed from the dietary ethyl palmitate. Work of this type has recently been reviewed in *Science Progress*.⁽³⁵⁾

Many applications of ^{15}N to the study of the metabolisms of proteins and amino-acids have been made and these have been reviewed by Rittenberg and Shemin.⁽³⁶⁾ Numerous papers dealing with the use of ^{13}C as a tracer in the study of fatty acid metabolism, etc., have been published in the *Journal of Biological Chemistry* from 1945 onwards.

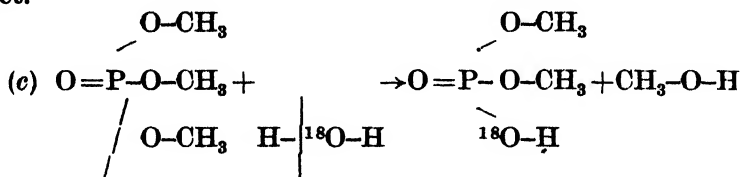
Applications of Heavy Oxygen.

The original investigation by Polanyi and Szabo⁽³⁷⁾ of the mechanism of alkaline hydrolysis of esters using the heavy oxygen isotope as a tracer element has been extended to investigations of the mechanisms of acid-catalysed hydrolysis of esters⁽³⁸⁾ and to acid-catalysed esterification reactions.⁽³⁹⁾ Urey and Roberts investigated the mechanism of the acid-catalysed esterification reaction between benzoic acid and methyl alcohol labelled with heavy oxygen. The reaction may occur via the mechanisms illustrated by the following equations:

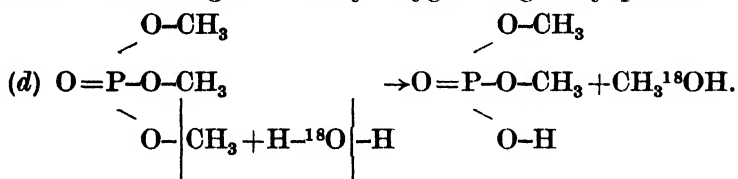


If the reaction occurs by a fission of the bonds, as is illustrated by the dotted lines in equation (a), water of normal isotopic composition would be produced. Mechanism (b), on the other hand, would yield water containing the heavy oxygen originally present in the alcohol. Experiment shows that water with a normal isotopic ratio is produced during esterification, and thus mechanism (a) is correct.

An investigation of the mechanism of hydrolysis of trimethyl phosphate,⁽⁴⁰⁾ the only inorganic ester so far considered, shows that under alkaline conditions behaviour is the same as for organic esters—the alkyl-oxygen bond remains intact.

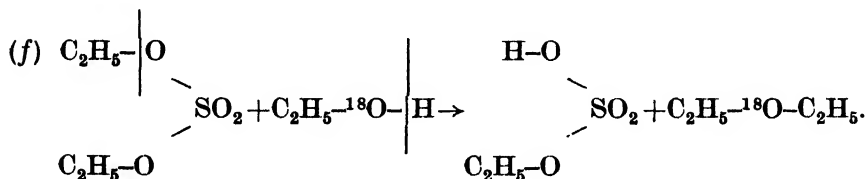
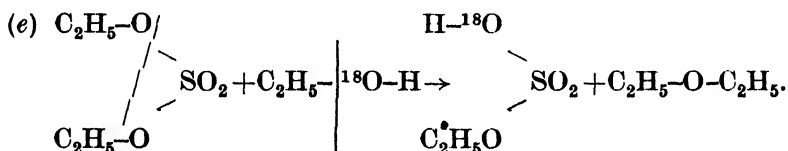


Under acid conditions, however, the result is not so clear cut. If the bonds break as is shown by the dotted lines in equation (c), the alcohol formed would contain normal oxygen. The other possibility at which a break may occur is shown by the dotted lines in equation (d); and this would lead to the formation of alcohol containing the heavy oxygen originally present in the water.



The experimental results show that both mechanisms are involved during acid hydrolysis or alternatively that the investigation is upset by the occurrence of certain side reactions.

Recently, the mechanism of formation of diethyl ether⁽⁴¹⁾ by reaction between diethyl sulphate and ethyl alcohol has been studied by use of heavy oxygen. In this reaction an alkyl-oxygen bond must break in one of the reagents. The two possible mechanisms are shown by equations (e) and (f).

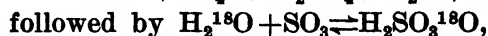


Experiment showed that the ether formed contained less heavy oxygen than the original alcohol. This dilution was attributed indirectly to the occurrence of two side reactions, namely hydrolysis and alcoholysis. The mechanisms of these reactions had not been investigated, and so their influence was eliminated by variation of the length of the reaction time. On extrapolation of the curve obtained by plotting ^{18}O -content of the ether against time, the ^{18}O content of the ether formed from the alcohol originally present in the mixture was obtained. This showed definitely that the ether was formed via mechanism (f).

The mechanisms of the benzil-benzilic acid rearrangement⁽⁴²⁾ and the Beckmann rearrangement,⁽⁴³⁾ as well as the alkali fusion⁽⁴⁴⁾ of certain organic compounds, have been studied by the use of heavy oxygen.

On the inorganic side, most of the applications of heavy oxygen have been for the determination of the rate of exchange of oxygen between water and the various oxy-acid ions.⁽⁴⁵⁾ In general, exchange occurs in acid solution, often in

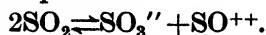
neutral solution and less frequently in alkaline solution. The mechanism of exchange in such reactions may involve addition and subsequent removal of a water molecule or hydroxyl ion to the anion, while in the case of the acid-catalysed exchange the most satisfactory mechanism appears to be reversible anhydride formation. For example, in the acid-catalysed exchange of oxygen between water and sulphate ions the following equilibria are believed to be involved :



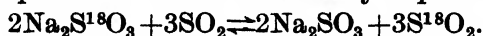
and so on until complete exchange is established.

Some mention may be made of the oxygen tracer work at present under investigation at the University of Queensland.

Jander's theory⁽⁴⁶⁾ of reactions in liquid sulphur dioxide is based on the idea that liquid SO_2 ionises to a small extent giving rise to sulphite ions and thionyl ions according to the equation



Recently Ingold and co-workers⁽⁴⁷⁾ have questioned the validity of certain of Jander's conclusions. It occurred to us that some useful information might be obtained by determining whether or not exchange of oxygen occurs between liquid sulphur dioxide and a dissolved alkali metal sulphite labelled with heavy oxygen. The above equilibrium would necessarily require an exchange to occur.



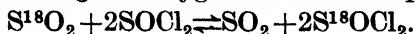
Jander gives the solubilities of various alkali metal sulphites as varying from 16 to 32 mg. per 100 gm. of SO_2 , but we cannot verify these figures. We have investigated the solubilities of the sulphites of sodium, potassium and ammonium as well as several other sulphur oxy-acid salts of these elements, but find virtually no solubility at all for any of these salts. We have used sulphur dioxide which has been dried very thoroughly and also sulphur dioxide containing small traces of water, but without any affect on the solubility.

It would be possible to carry out the exchange investigation by shaking liquid sulphur dioxide with the solid sulphite labelled with heavy oxygen, but it is preferable to use a sulphite which shows some degree of solubility.

While the original exchange investigation is held up pending the results of our solubility investigations, the possibility of exchange of oxygen between liquid sulphur dioxide and thionyl chloride is being investigated. According to Jander, thionyl chloride ionises in liquid SO_2



and, if SO_2 ionises, an exchange of oxygen would be expected.

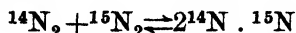


Another problem being investigated is the interchange of oxygen between metal oxides and oxygen gas. There have not been many applications of isotopes to the study of chemical reactions in solids and it is expected that this type of work will have important bearings on the theory of such reactions. In addition to obtaining exchange results at various temperatures and pressures it will also be necessary to determine such factors as dissociation pressures of the oxide at various temperatures, surface area of oxide prepared under varying conditions and also dissociation of oxygen molecules on the surface of the oxide. Little is known about these various factors, and thus in this field alone there is sufficient research to keep several investigators occupied for quite some time.

Applications of Heavy Nitrogen and Heavy Carbon.

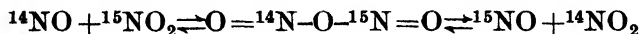
In the presence of a synthetic ammonia catalyst exchange between deuterium and ammonia occurs freely even at room temperature, leading to the formation of the substituted ammonias NH_2D , NHD_2 and ND_3 . Taylor and Jungers⁽⁴⁸⁾

from these results conclude that, at the temperatures used in the synthetic ammonia process, the rate controlling step is probably the dissociation of nitrogen molecules to atoms on the surface of the catalyst. This view was confirmed by showing that the equilibrium



is only slowly established on synthetic ammonia catalysts.⁽⁴⁹⁾ The reaction rate first becomes measurable at 450° C.

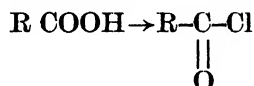
An interchange of nitrogen between nitric oxide and nitrogen dioxide in the gaseous phase at 2.5 cm. Hg pressure and -35° C. occurs at a very rapid rate.⁽⁵⁰⁾ This is presumably accounted for by the intermediate formation of nitrogen trioxide.



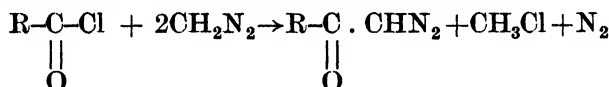
The chances of breaking either the $^{14}\text{N}-\text{O}$ bond or the $^{15}\text{N}-\text{O}$ bond would be about equal and the fission of the latter bond would lead to exchange.

The heavy carbon isotope, ^{13}C , has been used to study the Arndt-Eistert reaction.⁽⁵¹⁾ This reaction is used for the conversion of a carboxylic acid to its next higher homologue and it involves three stages :

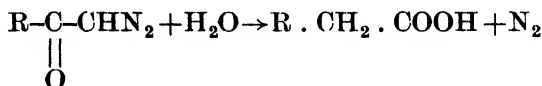
(i) Formation of the acid chloride :



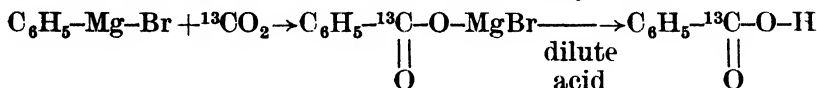
(ii) Reaction of the acid chloride with diazomethane :



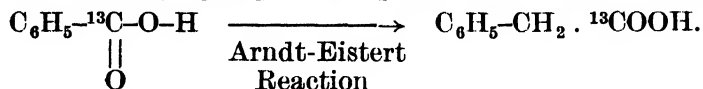
(iii) Rearrangement of the diazoketone with water in the presence of colloidal silver :



The problem to be decided is whether the carbon atom of the $-\text{COOH}$ of the original acid becomes the carbon atom of the $-\text{COOH}$ group of the final acid. This was demonstrated as follows : Benzoic acid containing an excess of ^{13}C in the $-\text{COOH}$ group was prepared by reaction between phenyl magnesium bromide and carbon dioxide labelled with heavy carbon.



After carrying out the Arndt-Eistert reaction the heavy carbon was found associated with the carboxyl group of the phenyl acetic acid formed.



The significance of this demonstration in connection with the mechanism of the reaction is discussed in the original paper.

Applications of ^{18}O , ^{13}C and ^{15}N to Analytical Problems.

The per cent. oxygen content of an organic compound is usually obtained by deducting the percentages of all other elements present from 100. Thus any errors in the estimations of other elements present will affect the accuracy of the estimation of the oxygen. A direct method of estimation of oxygen has recently been introduced by making use of heavy oxygen.⁽⁵²⁾

A few milligrammes of the organic compound are burnt with a definite amount of oxygen containing a known excess of ^{18}O . The dilution of the heavy oxygen by the normal oxygen originally present in the compound is then determined. The results are then sufficient to enable the per cent. oxygen to be calculated. Using oxygen containing about 2% ^{18}O , the oxygen contents of acetic acid, formic acid, nitro-methane and diethyl ether respectively were obtained within $\pm 3\%$. This accuracy is not all that might be desired, but by improving the technique or by using oxygen containing a larger proportion of ^{18}O the accuracy could be improved.

The same type of procedure has been applied to the estimation of carbon⁽⁵³⁾ and of nitrogen⁽⁵⁴⁾ in organic compounds. With the higher percentages of ^{13}C and ^{15}N available the estimated values showed a lower average error, namely $\pm 0.3\%$.

CONCLUSION.

Although isotopic tracer work has been in progress for a comparatively short time, it may be seen from the examples considered that much has been added to our knowledge of the way in which many chemical reactions occur. In certain cases this new knowledge could not have been gained other than by the use of a separated isotope as a tracer element.

It is, perhaps, fortunate that for the elements H_2 , N_2 , O_2 and carbon which play such an important part in the chemistry of everyday processes the stable isotopes may now be separated by comparatively simple means as these have proved more useful as tracers than the corresponding radio-active isotopes.

The measurement of the isotopic composition of a sample of oxygen or of hydrogen is readily carried out by the accurate measurement of the density of water formed from the sample. For carbon and nitrogen, however, the measurement requires the use of a mass-spectrograph. The absence of this latter equipment, which is highly expensive, is probably the limiting factor to the uses of the heavy isotopes of carbon and of nitrogen in Australian universities. This, perhaps, is unfortunate, as these two isotopes would appear to be of particular value to the study of the mechanisms of many organic reactions.

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OCCURRENCE OF THE BRACHIOPOD GENUS *PLECTODONTA* KOZLOWSKI AT BOWNING, NEW SOUTH WALES.

By IDA A. BROWN.

With Plate XIV and one text-figure.

Manuscript received, July 28, 1948. Read, September 1, 1948.

ABSTRACT.

Small fossil brachiopods occurring in the Hume Series in the Yass-Bowning district in N.S.W. are shown to belong to the Silurian genus *Plectodonta* Kozłowski; these specimens had previously been referred by Mitchell (1923) to the Devonian genus *Stropheodonta* Hall.

INTRODUCTION.

The reported occurrence of *Stropheodonta* spp. by Mitchell (1923) from fossiliferous beds at Bowning, N.S.W., has led to doubt of the Silurian age of the rocks in which these fossils were found. On account of the awakened interest in Upper Silurian and Lower Devonian palæontology and stratigraphy by workers in New South Wales and Victoria at the present time, it has been deemed advisable to investigate the validity of Mitchell's generic identifications in the light of more recent palæontological work in other parts of the world.

I am greatly indebted to Dr. G. A. Cooper, of the U.S. National Museum, Washington, D.C., for his kindness in permitting my use of the collections under his control and for other help and advice in the study of Palæozoic brachiopods, and to Mr. H. O. Fletcher, of the Australian Museum, Sydney, for permission to re-examine Mitchell's specimens in his care.

FIELD OCCURRENCE.

Mitchell's specimens come from several well-defined zones in the *Hume Series*, a conformable series of limestones, shales and fine-grained tuffs, whose characters have been described recently (Brown, 1941, pp. 319-326).

The Hume Series is the uppermost member of a sequence of Silurian sediments that have been folded into an elongated basin or synclinal structure (see map, Brown, 1941, Pls. XIV-XV).

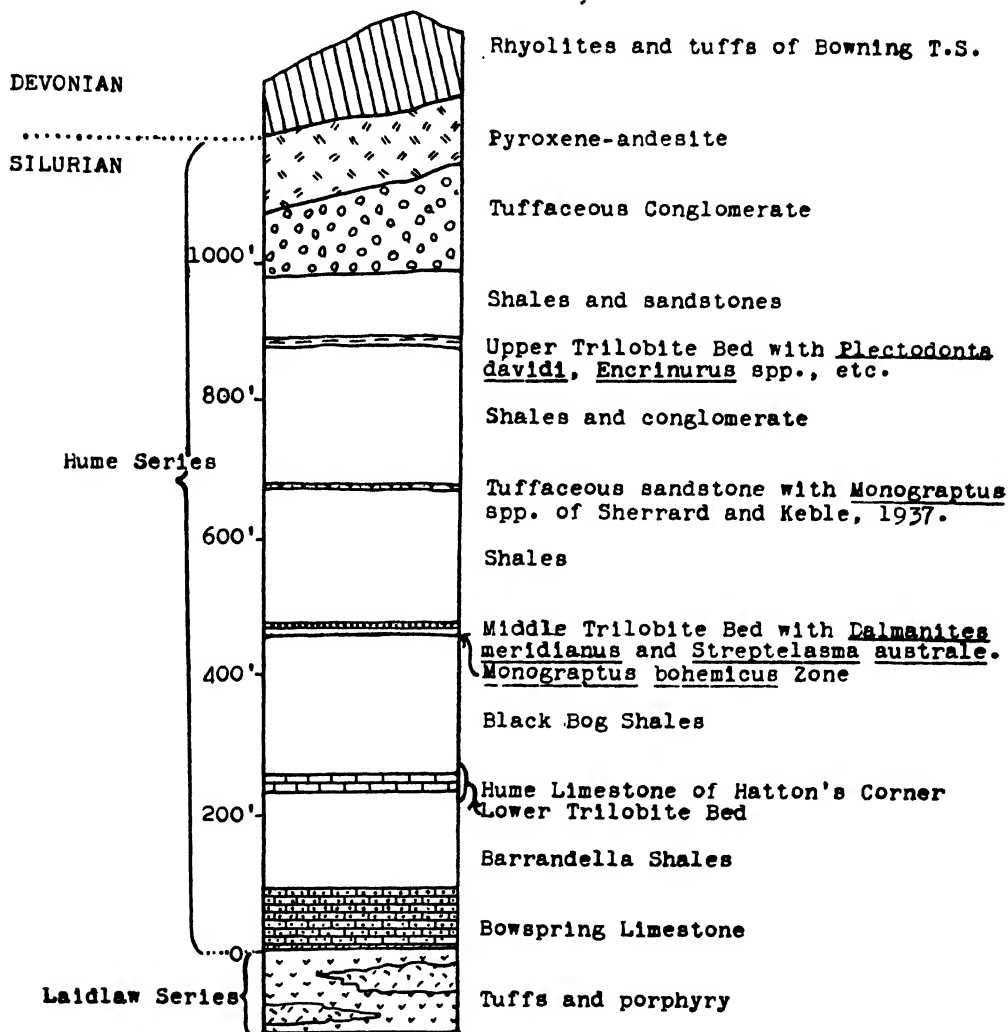
The folded series is overlain unconformably by a series of rhyolites and acid tuffs, which outcrop mainly to the west and south of the Yass-Bowning area, although outliers occur capping several different units of the Silurian sequence on Bowning Hill and also to the south of Yass. The rhyolites and tuffs belong to a petrographic province distinct from that of the Silurian of New South Wales, and are regarded as of Devonian age. They in turn are overlain, more or less conformably, by a series of shales and thin-bedded limestone containing Devonian fossils, which crop out along the valley of the Murrumbidgee River below Taemas Bridge, and whose stratigraphy and palæontology is being investigated at the present time.

The accompanying text-figure shows diagrammatically the sequence of Silurian beds in the vicinity of Yass and Bowning.

The Hume Series is richly fossiliferous throughout its lower portions, the Bowspring limestone, Barrandella shale and Hume limestone; the overlying Hume shale is not so prolific, but does include several graptolite (*Monograptus*

spp.) horizons both above and below the Dalmanites or Middle Trilobite Bed, and the Upper Trilobite Bed occurs near the top of the series.

Mitchell was well aware of the geological sequence in the vicinity of Bowning, and his published geological section (1888) in an east-west direction through Bowning Railway Station gives a faithful representation of the order of succession of the beds, although their dips are greatly exaggerated. Mitchell's "Lower Trilobite Bed" includes the Hume limestone (with its rich coral fauna of Hatton's Corner) and the shales immediately above and below.



Text-figure A.—Diagrammatic columnar section of the Silurian sediments in the vicinity of Bowning, New South Wales. Approximate thicknesses (in feet) are indicated for the section between Hatton's Corner and Bowning.

The accompanying table shows the stratigraphical distribution of Mitchell's species. All but three are from the Lower Trilobite Bed and are associated with undoubted Silurian fossils, well below the Monograptus beds. The remaining three of Mitchell's species were found in the Upper Trilobite Bed and these are specially considered in this paper. The only known outcrop of the Upper Trilobite Bed occurs under the Goods Shed at the eastern end of Bowning Railway

Station and along a small creek immediately to the south and east. The shales show conspicuous, rather highly-inclined cleavage but the true bedding-planes dip at angles of only about ten degrees. The fossils which have been recorded from this bed are listed in the paper to which reference has been made (Brown, 1941, pp. 330-332). These include 14 species of trilobites, three of *Conularia* and three of small brachiopods, which Mitchell referred to *Stropheodonta*. The trilobites include *Encrinurus* and other genera not known above the Silurian in other parts of the world; six of the species recorded from the Upper Trilobite Bed range upwards from lower beds. Mitchell's collections were made over the period of his twenty years' residence in the district and subsequent visits, but the collecting at most of his localities is now very poor.

Mitchell's Identifications.	Ventral Valve.	Dorsal Valve.	Geological Horizon.		
			L	M	U
<i>Stropheodonta bendenensis</i> Mitch.	×	—	L	—	—
<i>S. silverdalensis</i> Mitchell	×	—	L	—	—
<i>S. boreoides</i> Mitchell	?	×	L	—	—
<i>S. conica</i> Mitchell	×	—	L	—	—
<i>S. phalænoides</i> Mitchell	×	?	L	—	—
<i>S. transversa</i> Mitchell	×	?	L	—	—
<i>S. lilydalensis</i> Chapman (?)	×	—	L	—	—
<i>S. quadrata</i> Mitchell (non Calvin, 1878) ..	×	—	L	—	—
<i>S. incerta</i> Mitchell	—	×	L	—	—
<i>S. davidi</i> Mitchell	×	×	—	—	U
<i>S. minuta</i> Mitchell	×	×	L	M (?)	—
<i>S. bowringensis</i> Mitchell	—	×	L	—	—
<i>S. striato-costata</i> Mitchell	×	×	—	—	U
<i>S. striato-punctata</i> Mitchell	×	—	—	—	U
<i>S. fragilis</i> Mitchell	×	—	L	—	—

× = valve present.

— = valve not known.

? = uncertain.

U = Upper Trilobite Bed.

M = Middle Trilobite Bed.

L = Lower Trilobite Bed.

PALÆONTOLOGY.

The specimens described in Mitchell's paper (1923) consist of internal or external moulds, usually of single valves, as indicated in the accompanying table.

In the matter of generic determination Mitchell was evidently handicapped by the paucity of his material, by lack of comparative collections and by inadequate descriptions of genotypes in other parts of the world.

In recent years studies of the Stropheodontids have been published by Stainbrook (1938, 1943, 1945), Caster (1939), Cooper (1944) and Allan (1947). It is clear from these works, and from direct comparison with specimens in the collections in the U.S. National Museum, Washington, D.C., and elsewhere, that no true Stropheodontid is present among the Bowring specimens.

Apparently Mitchell was misled by the occurrence of a denticulate hinge into placing his specimens with the Devonian genus *Stropheodonta*, for Kozłowski (1929, pp. 112-113) and others have shown that denticulation is developed in several different stocks of the brachiopods, in the Stropheodontids (*Stropheodonta*), the Chonetids (*Eodevonaria*) and the Sowerbyellids (*Eoplectodonta* and *Plectodonta*).

Examination of Mitchell's specimens in the Australian Museum, Sydney, shows that they belong to the group of Sowerbyellids, described by Jones (1928), Kozłowski (1929) and others. The Sowerbyellids range through the Ordovician and Silurian in Europe and North America but rarely, if ever, continue into the

Devonian. The early forms in the Ordovician include *Sowerbyella* Jones (s.s.) ; later forms, in the early Silurian, possess denticulation along less than half the hinge, as in *Eoplectodonta* Kozlowski, while some of the succeeding forms in the Wenlock and Ludlow of England and the Borszczów stage of the Silurian of Poland, develop denticulation along the greater part of the hinge, as in *Plectodonta* Kozlowski.

The Bowring specimens from the Lower Trilobite Bed appear to belong to the genus *Eoplectodonta* Kozlowski, and those of the Upper Trilobite Bed should clearly be included in *Plectodonta* Kozlowski.

With regard to specific determinations I consider that there is insufficient evidence for erecting the number of species which Mitchell proposed. Of the three species from the Upper Trilobite Bed, all of which occur at the one locality, one (*P. davidi*) is represented by two specimens of internal moulds of conjoined valves and two separate internal moulds of single valves ; another species (*P. striato-costata*) is represented by a single valve and a specimen of an external mould of both valves and the third species (*P. striato-punctata*) by an external mould of a single ventral valve. I consider that the first two are probably conspecific and the third possibly also conspecific with these.

Of the rest of his material only one species (*S. minuta*) is represented with certainty by both valves, and this appears to be simply a very small immature shell. All other ten species described and figured by Mitchell come from the Lower Trilobite bed ; they are all represented by moulds of single valves only and probably represent variations of but a few species. Much more material is necessary for adequate determination.

No holotypes were designated in Mitchell's publication, but the illustrated specimens are identified in his handwriting on the Australian Museum labels and the holotype chosen in the present paper is in conformity with his indication.

SYSTEMATIC DESCRIPTION.

Superfamily STROPHOMENACEA Schuchert, 1896.

Family PLECTAMBONITIDÆ O. T. Jones, 1928, emend

R. Kozlowski, 1929.

Genus *Plectodonta* Kozlowski, 1929.

Genotype : *Plectodonta mariae* R. Kozlowski, " Les Brachiopodes Gothlandiens de la Podolie Polonaise ", *Palæontologia Polonica*, T.1, Warszawa, 1929, p. 114.

Small, transverse wide-hinged, concavo-convex Strophomenacea, ornamented with fine radiating costellæ. Hinge denticulate for the greater part of its length. In the ventral valve, a short median septum, bifurcating anteriorly ; the dorsal valve with two pairs of septa and a trilobed cardinal process.

Distinguished from *Sowerbyella* O. T. Jones (s.s.) by the denticulate hinge.

Plectodonta davidi (Mitchell).

(Plate XIV, Figs. 1-6.)

Stropheodonta davidi Mitchell, 1923 : *Proc. Linn. Soc. N.S.W.*, Vol. xlviii, Part 4, 1923, p. 470, Pl. XLI, Figs. 19, 20, 21.

S. striato-costata Mitchell : *Ibid.*, p. 472, Pl. XLII, Figs. 29, 30.

(?) *S. striato-punctata* Mitchell : *Ibid.*, p. 472, Pl. XLII, Fig. 31.

Holotype.—Aust. Mus. Coll., F.28749 ; Plate XIV, Fig. 1a.

Topotypes.—Aust. Mus. Coll., F.29383, F.28755 (internal mould of ventral valve), F.28754 (internal mould of dorsal valve).

Description.—Shell concavo-convex, semi-elliptical, small ; length of holotype, 3.7 mm. ; width, 6.0 mm. Other specimens are even smaller.

P.—September 1, 1948.

The holotype is an internal mould of both ventral and dorsal valves, opened out into approximately one plane. Traces of finely costellate, radiating ornamentation are indicated near the margins of the internal mould, there being 24 radiating costellæ in each valve. Shell structure pseudopunctate. The hinge is as wide as the shell. Delthyrial and notothyrial characters are somewhat obscure; primary teeth and sockets are small and divergent, and denticulations occur along the greater part of the hinge-line, but the hinge is not holodenticulate. A short median septum in the ventral valve bifurcates anteriorly. The cardinal process has at least two lobes and appears to be fused to the brachial processes. The dorsal interior shows two strong septa extending at least two-thirds of the radius of the shell, flanked laterally by shorter septa and several radiating rows of tubercles. The muscular areas are relatively large (see Plate XIV, Figs. 1, 2). Pallial markings are not known for *P. davidi* but a specimen of *Plectodonta bendeninensis* (Mitchell) from the Lower Trilobite Bed shows the pallial markings clearly and is illustrated in Plate XIV, Fig. 7.

Geological Horizon.—Upper Trilobite Bed, Hume Series.

Locality.—Bowning Railway Station, N.S.W. Coll. J. Mitchell.

Discussion.—The Bowning specimens closely resemble one (No. 84344) in the U.S. National Museum, Washington, D.C., of *Plectodonta maria* Kozłowski from the Borszczów stage of the Silurian of Uście Biskupie-Chudykowce, Poland, identified and presented by R. Kozłowski. A photograph of the latter specimen, kindly taken by Dr. G. A. Cooper, is reproduced on Plate XIV, Figs. 8 and 9, for comparison with the Bowning specimens.

There are also resemblances to other specimens in the U.S. National Museum and Sydney University collections of *Leptaena transversalis* Dalm (pars.), which has been referred by later authors to *Plectambonites*, *Sowerbyella* or *Plectodonta* (see O. Holte dahl, 1915; O. T. Jones, 1928, pp. 509–511; and Cooper, 1944, p. 335). These specimens come from various localities in the lower Gothlandian of Gotland; the Upper Llandovery beds of River Severn, Wales; the Wenlock Shales of Dudley, England; and from the Silurian of North America. Some of these specimens, whilst showing all of the other essential characters of *Plectodonta*, possess a hinge with denticulations along only half the length of the cardinal border, and by Kozłowski's definition should therefore be referred to his genus *Eoplectodonta*. The majority of these specimens have ventral valves that are more convex than those of the species from the Upper Trilobite Bed of Bowning.

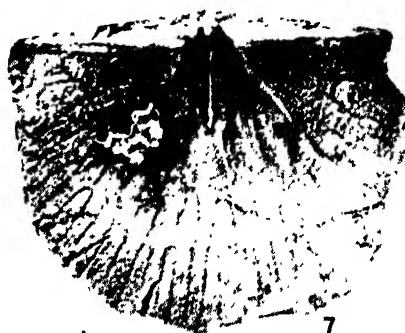
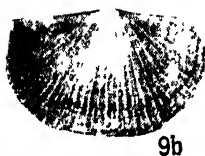
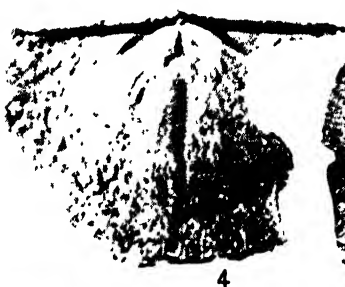
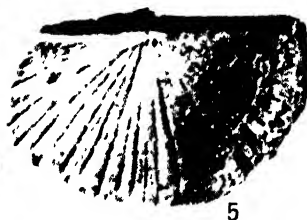
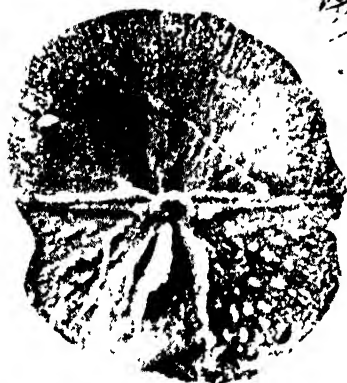
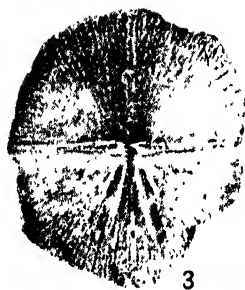
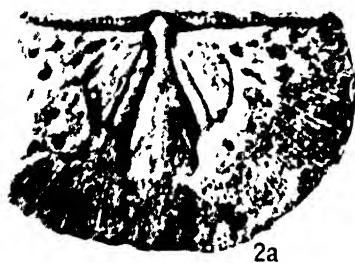
GEOLOGICAL AGE.

The stratigraphical evidence at Bowning indicates that the Upper Trilobite Bed containing *Plectodonta davidi* (Mitchell) is closely related to the underlying Silurian sediments and is separated from the Devonian beds by a major structural break.

The species most like *P. davidi* occurs in the Polish sequence, the Borszczów stage of the Gothlandian, correlated by various authors either with the top of the Lower Ludlow or within the Upper Ludlow of the English succession (see Kozłowski, 1929, p. 23).

The partially denticulate *Sowerbyella* and *Eoplectodonta* come from the Ordovician or the lower part of the Silurian of Europe and North America.

Thus *Plectodonta davidi* (Mitchell) (hitherto referred to the genus *Stropheodonta*) confirms the evidence of the associated fauna of the Upper Silurian (possibly Ludlow) age of the Upper Trilobite Bed at Bowning, N.S.W.



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EXPLANATION OF PLATE XIV.

All photographs are from untouched negatives; specimens were coated with ammonium chloride. Specimens figured 1 to 6 are all from the Upper Trilobite Bed at Bowning, and are now in the Australian Museum, Sydney.

Figs. 1-4.—*Plectodonta davidi* (Mitchell).

- 1a. Holotype, F.28749. A natural internal mould of both valves. Mag. ×6. Photo I.A.B.
- 1b. A rubber cast taken from the holotype (Fig. 1a) to show internal characters of both valves. Mag. ×6. Photo I.A.B.
- 2a. Topotype, F.28745. A natural internal mould of a dorsal valve. Mag. ×6. Photo I.A.B.
- 2b. A rubber cast of specimen (Fig. 2a) showing the internal structures of the dorsal valve; cardinal process fused to the brachial processes, denticulate hinge, two pairs of septa, large adductor scar areas and radial ornamentation. Mag. ×6. Photo I.A.B.
3. Rubber mould of topotype, F.29383. Conjoined valves similar to the holotype. Mag. ×6. Photo G. A. Cooper.
4. Topotype, F.28755. A natural internal mould of the ventral valve, showing bifurcating median septum. Mag. ×6. Photo I.A.B.

Figs. 5-6.—*Plectodonta davidi* (Mitchell) (= *Stropheodonta striato-costata* Mitchell).

5. Topotype, F.28748. A natural external cast of a dorsal valve. Mag. ×6. Photo I.A.B.
6. Topotype, F.28750. A natural external cast of conjoined valves. Mag. ×6. Photo I.A.B.

Fig. 7.—*Plectodonta bendeninsis* (Mitchell).

7. Loc. Lower Trilobite Bed near Bendenine Public School. A rubber mould of F.28788 (Aust. Mus.), A ventral valve showing pallial markings. Mag. ×3. Photo I.A.B.

Figs. 8-9.—*Plectodonta mariæ* Kozłowski, 1929 (84344, U.S.N.M. Coll.).

Loc. Uscie Biskupie-Chudykowce, Poland. Silurian (Borszczów Stage).

8. Portion of slab of rock showing complete specimens and internal of dorsal valve. Mag. ×2½. Photo G. A. Cooper.
- 9a. Dorsal view and 9b ventral view of complete specimen showing external ornamentation. Mag. ×2½. Photo G. A. Cooper.

STRUCTURAL DATA FOR THE NORTHERN END OF THE STROUD-GLOUCESTER TROUGH.

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With Plate XV and two text-figures.

Manuscript received, June 20, 1948. Read, September 1, 1948.

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INTRODUCTION AND PREVIOUS INVESTIGATIONS.

The Stroud-Gloucester Trough is one of the larger tectonic features of N.S.W., extending from the coastal country east of Raymond Terrace more or less meridionally to the latitude of Gloucester—a distance longitudinally through the Trough of about 65 miles. The main synclinal structure has been known to geologists for about one hundred years, as it is developed in country which was amongst the earliest to be settled in N.S.W., having been put to pastoral and mining use by the notable Australian Agricultural Company, which employed geologists and engineers to investigate the natural resources of its properties.

On account of the discovery of Permian coal eight miles to the north of Stroud, and later in the region between Stroud and Gloucester, considerable exploration was carried out in the country concerned, and it was early known to geologists that the coal measures were developed in a main basin twenty-five miles long (and possibly in a subsidiary basin) constituting the central part of the Trough, whose bounding structure was a double series of volcanic ridges, one series on the east and the other on the west.

F. Odenheimer described many salient features of the Basin in his Reports on the Geology and Mineralogy of the A.A. Co.'s Port Stephens Property (1855–1857). Later investigations by officers of the N.S.W. Mines Department (J. Mackenzie, 1875 ; T. W. E. David, 1887) extended knowledge of the Trough, and in 1907 Professor David described the Coal Basin between Ward's River and Stroud. Several further small reports appeared in the Reports of the Mines Department and in Jaquet's Memoir on the Iron Ore Deposits of N.S.W. (1901) reference to the earlier work was given.

It may fairly be said that no detailed work was done upon the northern part of the Trough until 1921, when C. A. Sussmilch described the general geology of the Gloucester District and discussed several interesting problems of the stratigraphy and structure of the Palæozoic rocks.

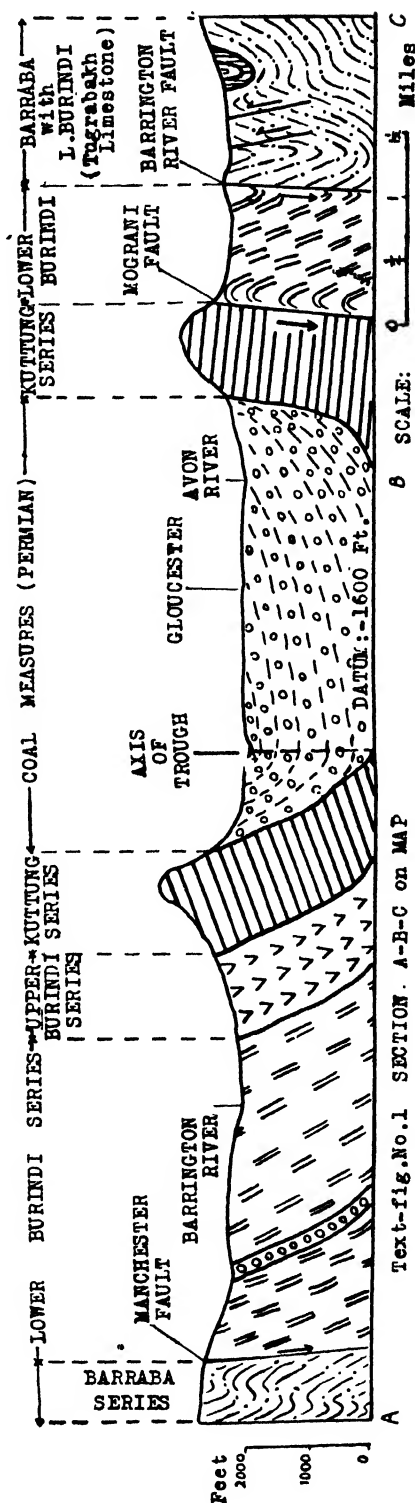
Sussmilch established the general Carboniferous sequence, and dealt with the relationships of this system to the Devonian and Permian Series, respectively. He was strongly of the opinion that the Devonian and Carboniferous were separated by an unconformity. He considered that the Coal Measures in the district were of Upper Permo-Carboniferous (Permian) age, and had been folded harmonically with the underlying Carboniferous, although a strong disconformity existed between the two groups. He emphasized the fact that the strong resistant lavas of the Kuttung Series made rugged ridges which were in great contrast with the subdued and low-lying topography of the central area given over to the Coal Measures.

To account for the behaviour of the outcrops of Palæozoic units, Sussmilch postulated and showed on his map a number of fairly powerful faults. While he considered these necessary to explain the structural features, he did not describe them, nor did he critically examine the zones of shatter.

In later years A. H. Voisey (1940) paid considerable attention to the area, particularly regarding the stratigraphy, and has made an important contribution. This may be said to have amplified and to some extent to have superseded the stratigraphical details given by Carey and Browne (1938) in an important paper summarizing the tectonics and other aspects of the Carboniferous System in eastern Australia.

Voisey, however, in his map, gave an imperfect picture of the structural relations of the region, but it must be pointed out that he was not vitally concerned with the tectonic problems.

In 1929 Osborne (see Bibliography) referred to the Stroud-Gloucester Trough when tracing the evolution of the trend-lines in the Hunter-Manning region, and



regarded the initial downwarping of the syncline as the earliest phase in the Late Palaeozoic (now called the Hunter-Bowen) orogeny (see 1929, pp. 456, 458, 460). In a later paper (1938), dealing with the southern end of the Trough, Osborne established some relations between two periods of faulting and the genesis of the Trough, and confirmed the earlier (1929) opinions and gave some details of the evolution of the Trough in its middle and southern portions.

In 1933, 1937 and more recent years, Osborne has spent considerable time mapping several features of the Gloucester-Rawdon Vale and Stroud areas, having noted and named the Rawdon Vale and Girvan Anticlines and the Waukivory Structure which flank the Trough on either side.

Faults postulated by Sussmilch, and minor structures in the Coal Measures of Weistmantels and Ward's River (in the central part of the Trough) were measured and these revealed that the Coal Series had suffered much more strongly than the Carboniferous lavas during the Upper Palaeozoic orogeny.

A considerable amount of stratigraphical work was also done in the Gloucester-Chichester-Monkerai region, but less attention was paid to the eastern side of the Trough. The researches of Voisey have made it unnecessary to pursue the study of the Carboniferous stratigraphy on the western side of the Gloucester area to any great extent, but the relations of this western segment to the areas lying directly southward are being investigated at the present time.

In 1947 P. B. Andrews devoted a considerable amount of time to a study of the Stratford-Gloucester district, paying most attention to the structural aspects, but also recording stratigraphical and physiographical data. A forthcoming paper will make available the results of his work in these last-mentioned branches, especially with regard to the eastern side of the Trough in this province.

The present paper is for the purpose of recording data pertinent to the tectonic study of the Trough, and represents a summation of observations over a long period by Osborne, and a recent intensive study by Andrews. The evolutionary aspects of the Trough's history in the Structural Plan of the Hunter-Manning-Myall Province is at present under preparation by the senior author, and these special aspects will not be traversed here. The map accompanying this paper has been prepared by Andrews. It incorporates more accurate mapping than has been done hitherto in the area. The study of the small-scale structures near Craven (which match those studied by Osborne further south) is the work of Andrews.

GENERAL SHAPE OF THE TROUGH.

As shown in the section (Text-figure 1), the Trough is marked by steep dips on both sides and an asymmetry which helps to produce such a wide alluviation of the valley excavated between the lines of meridional Carboniferous highlands. This asymmetry is clear from a study of the dips (see map), especially in cross sections such as that available from detailed examination of outcrops near the Buckets Road in the neighbourhood of the Gloucester River. It seems clear to the authors that the Coal Measures are mostly in normal contact with the Carboniferous floor, although disconformable in several places. They do not appear to be faulted against the resistant Carboniferous margins of the Trough, in the northern sector. However, faulted junctions do occur further south.

The axis of the Trough is decidedly to the west of the central geographic plane of the structure, and lies more or less along the course of the Gloucester River. Little can be found out regarding the plunge of the axis, but it is clear from the southward dips in the environs of the town of Gloucester that the northern part of the Trough is marked by a notable southward pitch. We must not overlook, however, the effect of the Barrington River Fault which throws to the south and shuts off the Basin on the northern margin. It is interesting to note that Odernheimer recorded the southerly plunge, basing his opinion on the examination of dips west and north of Gloucester.

The Trough is bordered, east and west, by powerful faults which are parallel to the significant lines of strike of the major fold. One of us (G.D.O.) has given evidence of the probable early relationship of these faults to the major fold in the Trough.

FAULTS.

General.

These may be divided readily into major and minor groups. Many of the latter are associated with the small-scale crumpling of the Coal Measures, while some are genetically related to certain of the major fractures.

The major set are again divisible into

- (a) Meridional faults cognate with the early Trough-fold.
- (b) Approximately east-west faults younger in age than (a).

Studies of small-scale fractures in quarries and elsewhere (many of which are results of the earlier survey) have been used as pointers to the tectonic environment existing in the larger areas of the Trough. These minor structures show a great contrast in evolutionary character. The following brief statements indicate the types of strain and fracture-pattern which occur in diverse manner through the brittle rocks examined :

- (a) Compression joints associated with small thrust faults have been observed striking within the interval N.N.W.-N.W. and dipping at moderate or low angles to both N.E. and S.W.
- (b) Closely packed tension joints, sympathetic with steep normal faults, mostly trending north and south, or at a small angle thereto.
- (c) High angle shear-joints in systems were measured in the earlier survey in the area between two of the larger east-west faults. These point to two possible alternatives for the origin of the larger faults (see below).
- (d) Slickensides on almost vertical planes bordering normal faults point to a movement along them at a time subsequent to the original faulting.

Description of the Faults.

Major Group. (a) *Those with a N.-S., N.N.W. or N.N.E. Strike.*

The Manchester Fault. This fracture is revealed by close study of the country between the Rawdon Vale Road near Faulklands in the south and the Copeland Road in the north. Exposures a little north of the Berrico Road, between it and the Gloucester River, show the Barraba and Lower Burindi strata standing almost vertically and hading slightly to the west. Many joints run parallel to the fault, which is normal with downthrow to the east. The basal part of the Lower Burindi hereabouts contains a notable conglomerate horizon, and the fault has thrown the Burindi Series to the east and exposed—west of the fault—a low zone in the Barraba mudstones. On the Copeland Road the same type of jointing is seen.

The fault is responsible for the juxtaposition of the Lower Burindi and Barraba Series along the western sector of the Trough. The fault has considerable displacement but its geometrical features are not known. The possibility of this Manchester Fault being the northward continuation of the Williams River Fault (Osborne, 1938) must be considered.

The East Stratford Fault. This dislocation has a swinging strike and cuts obliquely across the Kuttung and Burindi strata on the east side of the Trough, about $4\frac{1}{2}$ miles from Stratford. The associated joints in this zone suggest that this fault is intimately related to the main synclinal structures, thus being a truly strike fault.

In summary, therefore, we note that the two bounding faults of the Trough are probably due to stress-relief following the early compression that produced the meridional fold-structure. After severe compression the rocks opened up in a period of tension which followed the overstraining of the area.

Minor Faults and Those of Intermediate Magnitude.

Osborne has measured several small faults which fall into one of the two following categories :

- (a) Those due to stress-adjustment after initial folding.
- (b) Those due to shearing as a result of the early compression.

Of those to be placed in group (a) we have to record several fractures to be seen in the Faulklands-Berrico sector. Under (b) we should probably record the fractures noted by Sussmilch at the northern end of the Trough and re-studied by Andrews and named by him the *Bowman Road Fault* and the *Kiaora Fault*. The former is related to a small thrust west of it, which thrust dips westerly as seen in a cutting on the Barrington Road. The latter is probably a thrust which is responsible for the eastern boundary of the sunken block of Permian Coal Measures.

The Bowman Road Fault can be followed from the Bowman River bridge to Portions 16 and 417, A.A. Co.'s Grant, where it truncates the well-known outcrop of the Gloucester Buckets volcanic series, where these rocks are beginning to thin a little and to take on an east-west strike.

The *Kiaora Fault* is complementary to the Bowman Road Fault, and like the latter has been cut off by the Barrington River Fault. The effect of these faults and erosion upon the downthrown block of Permian Coal Measures has been to produce a lateral shift of about $1\frac{1}{2}$ miles northward.

An inferred fault, of steep dip, which has not been named, is shown on the map, striking a little north of west, and lying to the east of the Tugrabakh Road, northward from its junction with the Krambach Road. This probable fault would explain the association of steeply dipping Middle Devonian (Tamworth) Series on the Tugrabakh Road, and Barraba mudstones and tuffs in the country immediately east of the road. These mudstones, which underlie the Tugrabakh limestone, are well exposed in the quarry beside the road junction. This fault would probably dip strongly to the east.

East-West System of Faults.

Sussmilch postulated the probable existence of a branched fault-system trending roughly east and west through a zone four miles long and lying about a mile north of Gloucester. This was regarded by him as a major dislocation-zone because it truncated the Trough and placed it against a Devonian terrain with strike utterly opposed to the meridional trend of the synclinal structure.

The present authors have examined this fault zone closely and independently, and Andrews has been able to map the fractures more accurately than shown hitherto, and to extend the main fault to the west. The two component fracture-surfaces are here named the Barrington River Fault and the Mograni Fault.

The Barrington River Fault. This is the master fault of the east-west system, and it truncates the northerly striking Bowman Road Fault and the Kiaora Fault. Its effects are seen on the Giro Road (Portion 77, Parish of Fitzroy), where it places Lower Burindi rocks against the Devonian strata, and thence it runs east and later south-east to the confluence of the Gloucester and Barrington Rivers, from which point it swings to an easterly strike again and separates (in this neighbourhood) Upper Kuttung on the south from Middle Devonian on the north. After crossing the railway line the fault is found placing

Tamworth Beds against the Lower Burindi (this being partly due to the Mograni Fault). Further east the fault brings Barraba Series again adjacent to Lower Burindi (which are on the southern side).

The quarry at the junction of the Krambach and Tugrabakh roads gives eloquent testimony of the intensity of stress that was operative in the formation of the Barrington River Fault. The rocks are practically vertical and severely jointed, and in places cut by minor faults.

Further east, for about five miles along the course of the fault, there is a general condition of very steep strata constituting small fractured "schuppen" with erratic orientation, caught between the marginal surfaces of the fault zone. Strata to the north of the fault are of Barraba age, dipping about N. 55 E. until meeting the "schuppen" zone, where more easterly strikes prevail. Strata south of the fault are of Lower Burindi age and dip steeply to the N.N.W. The segment of Lower Burindi rocks caught between the Barrington River Fault and the Mograni Fault shows much fracturing and some conjugate shear-joints.

Mograni Fault. This is best interpreted as a branch fault, as its individuality is lost at a point one-third of a mile east of the railway line (see map). From this point the trend of the fault is first E.S.E. and then S.E. This fault makes a clear-cut boundary to the Kuttung volcanic Series which are found curving north-westward to help closure of the Trough on the eastern side. The eastern course of the fault is confirmed by the behaviour of the strata exposed in a quarry near the Krambach Road at the foot of the Brushy Cutting.

North of the fault are Lower Burindi strata with dip to the N.W., while to the south a succession of Kuttung, Upper Burindi and Lower Burindi terrains is sliced off by the fault, these series varying in strikes which reflect again the curvature of the eastern side of the Trough.

In 1933 Osborne measured the section through the Mograni Cutting and found evidence of lateral movement along small steep fractures running more or less east-west. The relation of these to the dip of the flow-planes in the rhyolites indicated slipping of the small segments westerly, parallel to the Mograni Fault.

Faults of Medium Magnitude.

The Upper Avon Fault and a Probable Fault South of Cut Hill Road. In a zone three miles wide, about the latitude of Stratford and west of that village, the continuation of the western side of the Trough is interrupted by a change in strike and the presence of the Upper Avon Fault and a possible fault running through the volcanic ridges a little south of the Cut Hill Road.

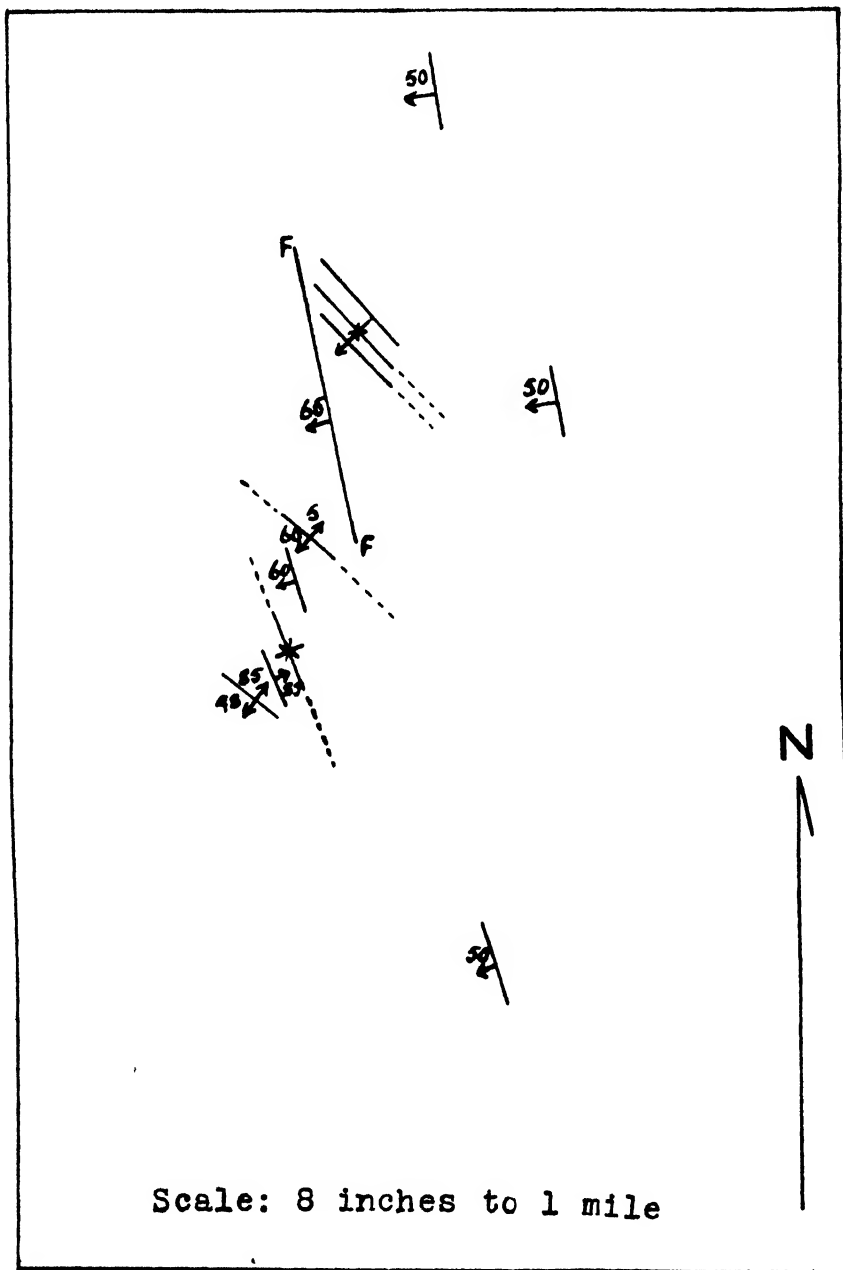
The latter fault appears to be present because of the truncation of outcrops (see map), but the authors have not been able to prove its existence to their entire satisfaction.

A bend in the strike of the west-side of the Trough from the usual meridional direction to approximately S.W. is related to movement of the west Stratford Block lying north of the Upper Avon Fault, which must have taken place during the later orogenic episode of the Upper Palæozoic diastrophism. This would give relief to other contiguous parts of the Trough, by the establishment of cross-faults.

In several parts of the area, and particularly in the district between the Turgabakh Road and the Barrington River, the Devonian strata are very intensely jointed, and most of the dips are unreliable. Careful consideration of the possible structural relations of the rocks is hampered by the ubiquitous steep (mostly vertical) and erratically trending strata.

RELATIONS BETWEEN THE MORE IMPORTANT FAULTS.

The two systems of faults present in the area seem susceptible of satisfactory interpretation when the course of the Hunter Bowen orogeny is considered. One of us (G.D.O.) has dealt with some aspects of this problem.



Text-fig. 2. Minor Folding near Craven

The Barrington-Mograni Fault System has truncated the Bowman Road and Kiaora Faults (N.-S. system) and thus is of later development. These

faults in the north of the district are cognate with the Upper Avon and associated fractures farther to the south. The southern group, and possibly the master faults to the north, may be along zones of shear associated genetically with the compression from the N.E. which assailed the Trough in the second phase of the deformation.

The whole genetic analysis and the evolution of the complete Trough are being considered by Osborne in the preparation of a monograph at the present time, and no further discussion is intended here, especially also since critical observations have yet to be made in the central sector of the Trough.

MINOR FOLDING NEAR CRAVEN.

The paucity of continuous outcrops in the Permian areas has made it difficult to map small folds, or to trace horizons in the Coal Measures. However, by means of railway and road cuttings, shafts and odd natural sections, a good deal of information that bears on the problems of the sequence of movements in the Trough is being assembled. Osborne has recently measured drag-folds and minor corrugations in the Ward's River sector.

Andrews, however, has made a special study of small-scale structure in the neighbourhood of Craven (see Text-figure 2).

DETAIL OF STRUCTURES.

The railway cuttings between Spring Creek and Craven reveal a number of interesting minor folds in the Coal Measures. At Spring Creek and along the Pacific Highway, about one-quarter of a mile east of the railway, the strata strike meridionally and dip at 50 degrees to the west. This is also the dip in Coal Creek, close to Craven Railway Station.

Along the railway line, however, about three-quarters of a mile north of Spring Creek, the strata are seen to strike N.W. and to dip S.W. at 48 degrees. Just north of this first exposure an anticlinal axis appears, the strata to the north dipping E.N.E. at 85 degrees.

The dip of W.S.W. at 60 degrees in the next cutting north implies a synclinal axis between the two exposures. Farther north still there is another anticlinal axis.

In the cutting half a mile south of Craven Station there is a thrust fault dipping W. 10 S. at 60 degrees, causing drag-effects in the strata.

Immediately north of this fault is an anticlinal axis, striking N. 40 W. and plunging steeply to the N.W. Another 100 yards brings us to a similarly plunging syncline, which possesses drag-folds with axes parallel to the parent structure.

The fold axes described above are not parallel but trend within an interval of about 30 degrees, and intimate knowledge of neighbouring district shows that they are very local in development. They are interpreted as incompetent folds in weak Coal Measures within the major Trough-structure, and were caused by the pressure from the north-east.

CONCLUSION.

The descriptions given in this paper constitute a record of data obtained over a period of years by intermittent geological investigations by one of us, and by a recent intensive field-season by the other.

The evaluation of the various structural entities as criteria useful in diagnosing the evolutionary characteristics achieved by the Late Palaeozoic Orogenic Episodes has only been attempted in a preliminary way. Further research along these lines and the placing of the Stroud-Gloucester Trough in the

larger setting of the Hunter-Karuah province and its structural history are pressing problems now being prosecuted towards completion by Osborne.

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THE CONCEPTS OF RESISTANCE, CAPACITANCE AND INDUCTANCE IN THERMAL CIRCUITS.

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INTRODUCTION.

The analogy between the flow of heat under a temperature difference and the passage of an electric current under a potential difference is widely used as a teaching aid both to elementary students in physics and in the instruction, at a slightly more advanced stage, of chemical engineering students in aspects of heat transfer phenomena. Many examples of such a treatment could be found in such a standard reference book as McAdams (1942). The analogy has been given a quantitative significance by the definition of units of thermal current and thus of thermal resistance. Harper (1928) has proposed the name "fourier" for a unit of thermal resistance and White (1938) has defined a "thermal ohm" as that unit of thermal resistance which allows one watt of heat energy flow to be generated by a potential difference of one degree centigrade.

This analogy between electrical and thermal circuits has been made the basis of a model method of studying heat flow problems by the construction of equivalent electrical circuits. Langmuir, Adams and Meikle (1913) proposed such a method some thirty years ago, and it has since been developed to deal with transients as well as steady state flow. The principal authors concerned with this development have been Beukin (1937, 1938) and Paschkis (Paschkis and Beukin, 1938; Avrami and Paschkis, 1942; Paschkis and Baker, 1942; Paschkis and Heisler, 1946), and their method has been primarily concerned with the flow of heat in solid insulators. Since, as they claim, oscillatory phenomena are not observed in these heat flow problems, the thermal circuits are non-inductive and may be represented by electrical models consisting of resistances and capacitances. In heat flow through a continuous block of matter the resistances branch out in all directions and thermal capacities are distributed along the resistances. In the method of Paschkis and his co-workers the body in question is broken up into a number of sections, the resistances lumped between these sections along the co-ordinate axes and the capacitances to earth concentrated at the centres of each section. Even with a limited number of sections Paschkis has claimed considerable accuracy for models of this nature.

THE INDUCTANCE OF NATURAL CONVECTION CURRENTS.

An electric current flowing in any circuit is always associated with a magnetic field around that circuit. This field possesses a kinetic energy which has been "borrowed" from that of the electric current and as a result the electric current does not settle down immediately to a steady value if the e.m.f. is suddenly changed. That property of an electric circuit which measures the quantity of kinetic energy in the magnetic field associated with unit current is referred to as the (self) inductance of the (electric) circuit. The author (Bosworth, 1946) has claimed that the thermal circuits associated with the heat loss by natural convection in fluids show a property which could be called thermal (self).

Q.—September 1, 1948.

inductance. The process of heat flow sets up pressure differences which results in a flow of fluid as a convection current. The fluid flowing in the natural convection circuit possesses (mechanical) kinetic energy which has its origin in the energy of the thermal potential or temperature difference producing the heat flow. This kinetic energy bestows on the thermal circuit inductive properties. A method of demonstrating this property has been described. A device is set up capable simultaneously of measuring the heat flow from a body immersed in a fluid and the temperature difference between the surface of the body and a representative point in the fluid. At a stated time heat is suddenly supplied to the body at a steady rate and the temperature difference between the body and the fluid is measured as a function of the time giving a curve which is that of a thermal transient.

The apparatus which has been used for measurements of this nature consists of a short wire of resistance alloy, such as nichrome or constantan, to the centre of which is welded a sensitive thermocouple of fine wire. The other junction of the thermocouple is immersed in the fluid some 5 mms. from the surface of the alloy wire; so that the couple thus measures the temperature difference between the alloy wire and some point in the fluid. The alloy wire could be heated by an electric current. Since the wire was chosen to be of material of low temperature coefficient of resistance, the heat input may be taken as proportional to the square of the heating current. The temperature difference may likewise be taken as proportional to the reading of a galvanometer attached to the thermocouple. The theory of the use of instruments of this nature has been discussed by the author (Bosworth, 1944). A.C. is preferably used for the heating current as possible errors arising from electrolysis or from an unsymmetrical welding of the thermocouple elements are thus avoided.

If such an instrument is immersed in a fluid and at a time $t=0$ a current I is suddenly applied and the readings of the temperature difference (θ) are taken at intervals, the θ versus t plot takes a characteristic form. θ rises from zero at $t=0$ to a maximum value and then falls asymptotically to the final steady value from above. Figure 1 gives some illustrative curves for the transients from a 19 gauge S.W.G. nichrome IV wire. Curve A refers to a heating current of 12.6 amps. in toluene, curve B 12.6 amps. in ethanol, curve C 7.8 amps. in carbon tetrachloride, curve D 18.6 amps. in water, curve E 4.0 amps. in toluene, and curve F 2.5 amps. in carbon tetrachloride. Interpretation of these curves is easy. The system of convection currents possess inertia and take time to settle down to the final value. The rate of heat loss for a given temperature difference is less in the absence of the full convection current, and so with a given heat input the surface initially rises to a temperature higher than that attained when a steady convection flows past the hot wire. Curves similar to those shown in Figure 1 have been recorded in a letter to *Nature* (Bosworth, 1946). It is clear that this phenomenon means that in any attempt to represent heat flow phenomena in fluids by the Paschakis method of electric models the circuits must now involve inductances as well as capacitances and resistances.

Having found systems which show heat flow phenomena which can be described as *thermal self inductance*, the obvious next step would be to attempt to describe a system showing *thermal mutual inductance*. Suppose we take two wires welded to thermocouples and place them in a fluid in such a position that the convection current from one passes over the other. The wires, considered as heat circuits, are now linked by the inductive element, the convection current. Any change in the heat flow from one hot wire will alter the magnitude of the convection current and this will change the heat flow from the other wire. We regard the heat flowing from a hot wire to the fluid as proportional to the *thermal current* and the temperature difference as the thermal p.d. or the *thermomotive*

force. If *A* and *B* are two wires coupled by the same convection current, we may say that the system possesses the property of thermal mutual inductance if when the thermal current from *A* to the fluid is suddenly changed there is a transient change in the thermomotive force, or temperature difference, between *B* and the fluid. This property may be readily demonstrated. The following equipment was used in the demonstration.

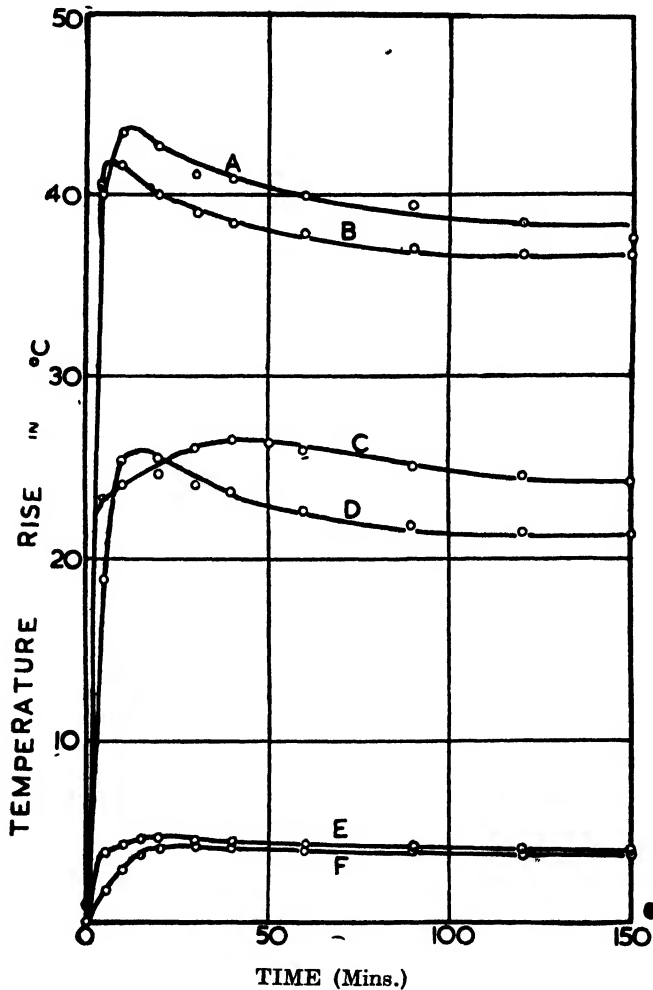


Fig. 1.

Two parallel wires of 22 gauge (S.W.G.) nichrome IV each attached to a fine copper-constantan thermocouple were set, one wire vertically above the other, in a fluid. The distance apart in the first experiments was 18 mms. and the first fluid used was distilled water. A heating current of 2.0 amps. was suddenly switched on to the lower wire, causing its temperature to rise by $10.5^{\circ}\text{C}.$, the temperature settling down to the final steady value within the period of swing of the galvanometer. The behaviour of the temperature difference between wire *B* and the fluid is represented by curve *A* in Figure 2. It will be observed that for a period of the order of a minute there is no change and then the temperature difference commences to rise, passes through a maximum of $0.52^{\circ}\text{C}.$ in 200 seconds and then falls slowly almost to zero again. Curve *B* on Figure 2 shows the effect of suddenly applying a current of 8.0 amps. to the lower filament

(producing a temperature rise of 70°C. between lower filament and fluid). In this case the initial period of no temperature change in the upper filament is reduced to 20 secs. The succeeding temperature rise is far steeper, the maximum of 4.6°C. being attained in 55 seconds. The return of θ to the final value was also more rapid in this case.

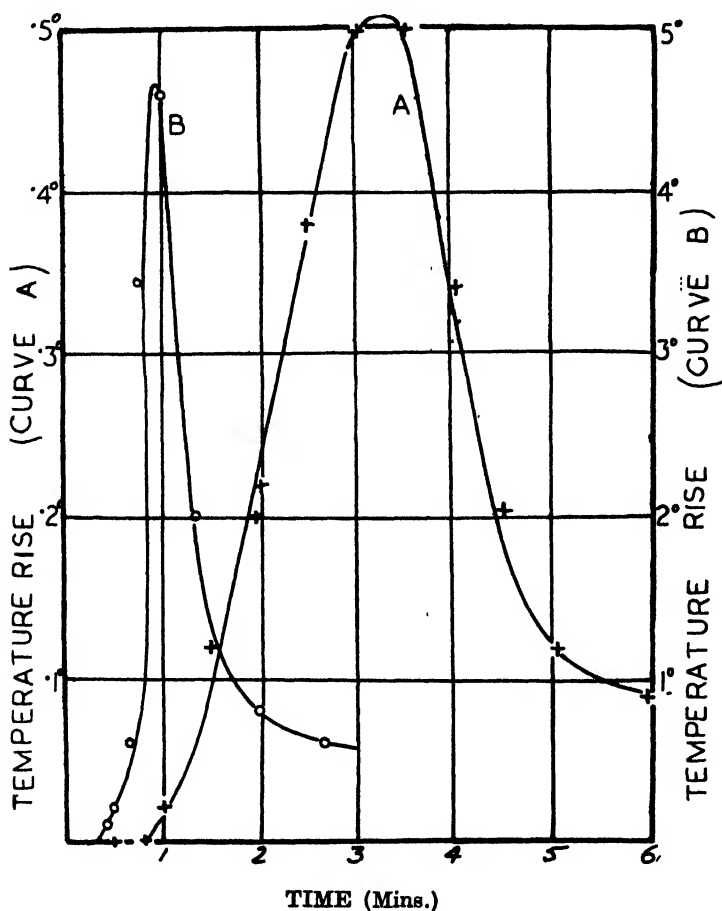


Fig. 2.

Transients of a considerably longer period are exhibited if the two filaments are immersed in a more viscous fluid. Figure 3 shows results obtained in a 75.2% sucrose solution at room temperature. The density of this solution was 1.3808 grammes per ml. and the viscosity 360 centipoises. Curve A refers to a heating current of 2.0 amps. producing a temperature rise of 43°C. in the lower wire and curve B to a heating current of 5.0 amps. producing a temperature rise of 140°C. in the lower filament. The transient thermal current induced in the upper filament has a much longer period in the former case. As far as these and similar experiments go then, the period of the transient is the longer the lower the primary temperature difference and the higher the viscosity of the fluid. This might have been expected, as the intensity of the convection current from any hot body in a fluid depends on the Grashof number which involve θ in the numerator and the viscosity in the denominator.

THE UNIT OF THERMAL RESISTANCE.

If we are to set up the equivalent electrical circuit to represent both the steady state and transient conditions obtained in the flow of heat in fluid systems careful thought must be given to the definition of the unit of thermal resistance. As claimed by the author (Bosworth, 1946*a*), the definitions of Harper and of White are not completely satisfactory. We may, however, proceed in the following way: We take the unit of thermomotive force as the degree centigrade and the unit of energy as the joule. Let us consider any length of a thermal circuit over which there is a temperature difference or thermal p.d. θ , and suppose that in a time dt a quantity of heat dQ (joules) flows through the circuit. Let the absolute temperature of the mid-point of the circuit be T . (θ will be assumed

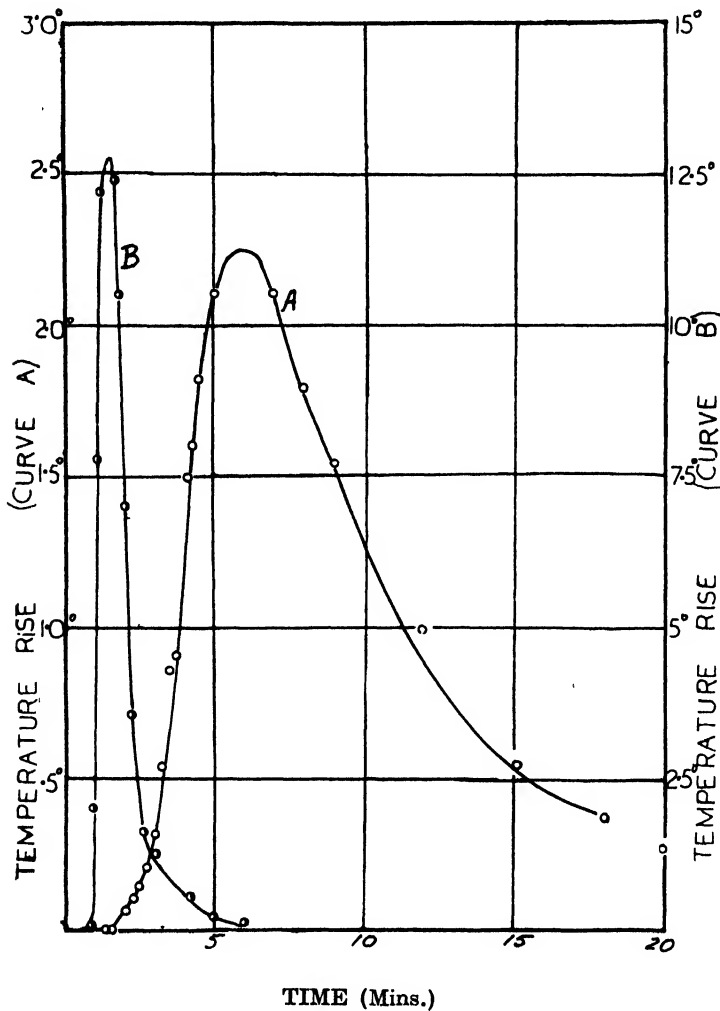


Fig. 3.

to be small in comparison with T). The work done by the flow of heat in the circuit follows from the second law of thermodynamics as

$$\frac{dQ}{T} \theta \text{ (joules).}$$

Now if I_q is the magnitude of the thermal current flowing, the work done by the current in the time dt will be

$$I_q \theta dt \text{ (joules).}$$

It therefore follows that

$$I_q = \frac{d}{dt} \left(\frac{dQ}{T} \right) = \frac{dS}{dt} \dots\dots\dots (1)$$

where S is the entropy gain of the sink.

If we refer to the unit of thermal current as defined by equation (1), it follows that the unit of thermal resistance, or thermal ohm, is that of a portion of a thermal circuit such that one degree centigrade produces a thermal current of one watt per degree centigrade. Consider a cylindrical conducting body of length l , cross sectional area a and of mean temperature T (degrees absolute). Let q be the quantity of heat transferred per unit area per unit time. The resistance in thermal ohms is then given by:

$$R_q = \frac{\theta T}{qa} \dots\dots\dots (2)$$

The specific thermal resistance, or resistivity (σ_q) of a given material may then be given by the expression

$$\sigma_q = R_q \frac{a}{l} = \frac{\theta T}{ql} = \frac{T}{q} \text{ grad } \theta \text{ or } \frac{T}{q} \text{ grad } T \dots\dots\dots (3)$$

In terms of equation (3) the specific thermal resistance of copper at 20°C . (293.1°K .) becomes

$$\sigma_q (\text{Cu}) = 75.6 \text{ thermal ohm cms.}$$

For water at the same temperature the specific thermal resistance becomes

$$\sigma_q (\text{H}_2\text{O}) = 48,600 \text{ thermal ohm cms.}$$

THE UNIT OF THERMAL CAPACITANCE.

In terms of the thermal current as entropy flow and the thermomotive force as temperature difference, a definition of unit thermal capacitance may be given in the following words:

A body has a capacitance of one thermal farad if an amount of entropy of one joule per degree centigrade added to that body raises the temperature by one degree centigrade.

Thus if a body of volume V has a temperature T and consists of matter of density ρ and specific heat at constant pressure c_p , its capacitance in thermal farads (at constant pressure) is

$$C_q = \frac{V \rho c_p}{T} \text{ (thermal farads)} \dots\dots\dots (4)$$

The capacitance of one ml. of copper at 20°C . on this basis amounts to

$$11.6 \text{ thermal millifarads}$$

and of one ml. of water at the same temperature

$$14.3 \text{ thermal millifarads.}$$

If a thermal capacitance C_q is charged by a thermal current I_q for a time dt , the resultant temperature rise θ is given by

$$\theta = C_q \int I_q dt \dots\dots\dots (5)$$

which on substitution in equation (1) gives

$$\theta = C_q \int \frac{dQ}{T} \dots\dots\dots (6)$$

The potential energy (P) stored during this process is given by

$$P = \frac{1}{2} \theta^2 / C_q \\ = \frac{1}{2} \theta \int \frac{dQ}{T} \dots\dots\dots (7)$$

which is an expression for the *available* thermal energy stored by charging the body concerned to a temperature θ above that of its surroundings.

THE UNIT OF THERMAL INDUCTANCE.

The thermal inductance of a system of convection currents may be most directly defined in terms of the temperature difference between solid surface and bulk fluid which is set up when the entropy flow is changing at a unit rate. An equivalent definition, perhaps more suitable to heat flow problems, may be expressed by the equation

$$L_q = \frac{2K_q}{I_q^2} = \frac{2K_q T^2}{(\dot{d}Q/\dot{d}t)^2} \text{ (thermal henries) } \dots\dots\dots (8)$$

where L_q is the thermal inductance and K_q is the kinetic energy in joules stored in the system of convection currents surrounding the hot body.

The calculation of K_q for a system of known dimensions has not yet, as far as the author is aware, been effected; but should not be extremely difficult. Meanwhile, an estimate of the value of L_q may be made from the form of the thermal transient. The relaxation time for a circuit involving resistances and inductances is equal to L/R . For the systems illustrated in Figure 1 this relaxation time is of the order 10 seconds. The thermal resistance per unit length of heated wire is of the order 15,000 thermal ohms. Accordingly the thermal inductance of this arrangement of a hot wire in water is of the order of 150 thermal kilohenries.

The inductances of thermal circuits is accordingly represented by considerably larger figures than the corresponding figures in electrical circuits.

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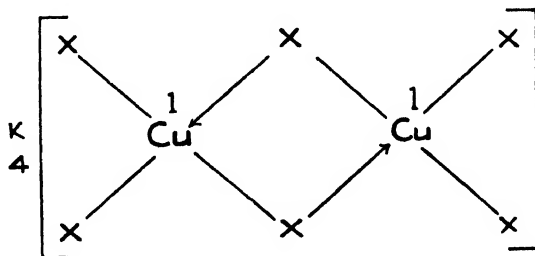
COORDINATION COMPOUNDS OF COPPER.

PART I. COMPLEX COPPER (II) CUPRATES (I).

By C. M. HARRIS.

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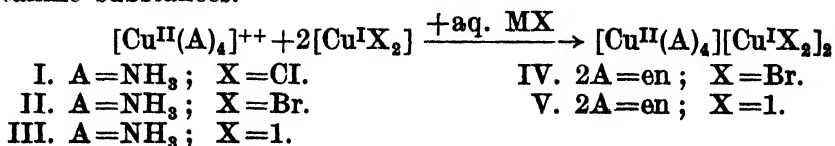
It is well known that copper (I) halides readily dissolve in concentrated aqueous solutions of alkali or ammonium halides, particularly on heating, to form clear solutions from which can be isolated the complex copper (I) halides $M[Cu^IX_2]$ and/or $M_2[Cu^IX_3]$ (where $M=K, Na$ or NH_4 , and $X=Cl, Br$ or I). The latter compounds are probably



bridged complexes as above, in which copper (I) is four covalent whilst in the other type the copper (I) atom is two covalent (Wells, 1945). Comprehensive lists of these compounds are given by Abegg (1908a) and Mellor (1923).

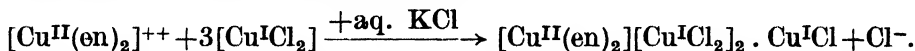
Many copper amines are reported throughout the literature, and, amongst the ammonia compounds, tetrammine and hexammine copper (II) halides are well known. The bis-ethylene diamine copper (II) halides, $[Cu(en)_2]X_2 \cdot H_2O$ ($X=Cl$ and Br) were prepared by Dubsy and Dostal (1932), and these together with the iodide were re-examined by Johnson and Bryant (1934) who gave evidence for the existence of the $[Cu(en)_2]^{++}$ ion in the solid state. Six covalent complexes $[Cu(en)_3]X_2$ (Dubsy *et al.*, 1932) have also been prepared and compounds of pyridine with copper (II) halides (see later) are known. Morgan and Burstall (1926) prepared the complex copper (II) dicyano cuprate (I) $[Cu^{II}(en)_2][Cu^I(CN)_2]_2$ whilst Souchay (1940) prepared the copper (II) dibromo cuprate (I) $[Cu^{II}(Pym)_2][Cu^IBr_2]_2$ with coordinated pyramidone.

In the present work a series of coordinated copper (II) dihalogen cuprates (I) containing ammonia and ethylene diamine as coordinating addenda have been prepared. The method consisted of the double decomposition of complex copper (I) halide in a concentrated solution of alkali or ammonium halide with a solution of the required copper (II) ammine also containing alkali or ammonium halide to avoid precipitation of copper (I) halide. By reacting two moles of copper (I) halide with one mole of a tetrammine copper (II) halide as above, complexes of the type $[Cu^{II}(A)_4][Cu^IX_2]_2$ have been obtained from solution as crystalline substances.



Compound I was obtained as the monohydrate if the mole ratio of copper (II) ammine to copper (I) chloride was 1 : 2 or 1 : 3 but the latter ratio was employed since it gave the best yield of product.

The ethylene diamine dichloro complex $[\text{Cu}^{\text{II}}(\text{en})_2][\text{Cu}^{\text{I}}\text{Cl}_2]_2$ was not isolated but instead the compound $[\text{Cu}^{\text{II}}(\text{en})_2][\text{Cu}^{\text{I}}_3\text{Cl}_5]$ was obtained. This compound is similar to the preceding compounds except that it contains an extra molecule of copper (I) chloride, and it is suggested that the extra molecule of copper (I) chloride is probably involved in the crystal lattice and the compound would be better represented as $[\text{Cu}^{\text{II}}(\text{en})_2][\text{Cu}^{\text{I}}\text{Cl}_2]_2 \cdot \text{Cu}^{\text{I}}\text{Cl}$ (VI). It was obtained if the mole ratio of copper (II) ammine to copper (I) chloride was 1 : 2 or 1 : 3. The latter ratio gave the best yield of the complex.



It is interesting to note that a compound $4\text{NH}_4\text{Cl} \cdot 3\text{Cu}_2\text{Cl}_2$ prepared by Wells and Hurlburt (1895) can also be formulated $(\text{NH}_4)_2[\text{Cu}^{\text{I}}_3\text{Cl}_5]$ and would appear to be the ammonium analogue of VI. Complex cyanides $\text{R}_2[\text{Cu}^{\text{I}}_3(\text{CN})_5]$ (where $\text{R} = \text{Rb}$ and Cs and $\text{R}_2 = \text{Ca}$) of similar formula to the above chloride have been prepared by Grossmann and Forst (1905).

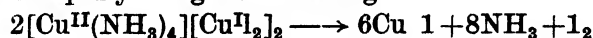
In the compounds which are now described copper (II) exhibits its usual coordination number of four and the copper (I) atom a covalency of two, at least, in compounds I-V inclusive.

The preparation of these compounds was first attempted with the iodide III at room temperature, but owing to the large amount of potassium iodide required to prevent precipitation of the copper (I) iodide on addition to the copper (II) ammine solution it was attempted at elevated temperatures and the product isolated on cooling. This was found to be generally more successful in that it yielded a purer product and required less potassium halide in solution. The copper (II) ammine was prepared *in situ* from the corresponding copper (II) halide or in some cases diammine copper (II) acetate by adding ethylene diamine in theoretical amount or ammonia in sufficient excess to stabilize the ammine formed. The use of copper (II) sulphate for this purpose was not satisfactory as it was found to contaminate the product with potassium sulphate. Heating of the copper ammine solution was carried out in a water bath to prevent superheating of the walls of the reaction vessel and local decomposition particularly of the ammonia compounds. The complex copper (I) halide solution was always added to the copper ammine solution. Compound I was prepared at a much lower temperature using ammonium chloride instead of alkali chloride as it was found to prevent the formation of basic salts during the reaction.

A compound described as a double iodide of copper and ammonia was prepared by Saglier (1886) by treating ammoniacal copper (II) oxide with alcohol and iodine. Abegg (1908*b*) formulated the compound as III, which it undoubtedly was. The method is not as good as that now described and the product does not appear from the analytical results to have been as pure. Ritt-hausen (1853) claimed to have prepared a blue compound containing copper (I) and copper (II) chloride, ammonia and water. He isolated the compound as one of the products of reaction of saturated ammonium chloride solution on copper in the presence of air and assigned to it the formula $\text{Cu}_2\text{Cl} \cdot \text{NH}_3 \cdot \text{CuCl} \cdot \text{NH}_3 \cdot \text{HO}$. However it has since been postulated by Abegg (1908*b*) as $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{Cl}_2]_2 \cdot 2\text{H}_2\text{O}$. More recently Burrows and Sanford (1935) suggested that it corresponds to the formula $\text{Cu}_2\text{Cl}_3(\text{NH}_3)_3\text{H}_2\text{O}$ one of the copper atoms being in the monovalent and the other in the divalent condition and that such a compound would be analogous to the arsine derivative $[\text{Cu}_2\text{Cl}_3[(\text{Ph}_2\text{Me})_3\text{As}]_3]^\circ$ described by them. The atomic ratio $\text{Cu} : \text{Cl} : \text{NH}_3$ calculated by them from R's analytical results as 1 : 1.34 : 1.37 would better

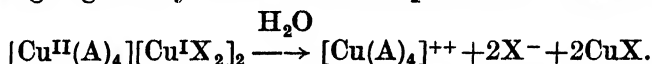
fit the formula $\text{Cu}_3\text{Cl}_4(\text{NH}_3)_4$ and from a consideration of its analysis, method of preparation, colour and reactions it would appear to have been the monohydrate I. The analytical results of Ritthausen's preparation are far too high for Abegg's postulated dihydrate. Compound I lost 3 per cent. of its weight on heating at $70-80^\circ\text{C}$., and this could not have been primarily due to ammonia since the ammonia content only decreased an amount equal to approximately 10 per cent. of the total loss. The compound similarly lost weight in a phosphorus pentoxide desiccator and in both cases the loss was accompanied by a colour change from violet to mauve. The loss is less than theory due to simultaneous absorption of oxygen and oxidation of copper (I) during the determination. The present method for the preparation of compound I is less ambiguous and more quantitative than that of Ritthausen.

The ammonia compound III slowly decomposes in the atmosphere, forming copper (I) iodide and liberates iodine and ammonia. The reaction proceeds to completion more rapidly on gentle heating

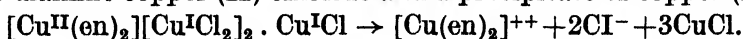


leaving a quantitative yield of copper (I) iodide. The atmosphere above the compound in a stoppered bottle yields positive tests for iodine and ammonia. Its ethylene diamine analogue does not behave similarly, due to the fact that the chelate group, ethylene diamine, forms much more stable compounds with divalent copper than does ammonia.

On shaking vigorously with water compounds II-V are decomposed thus :



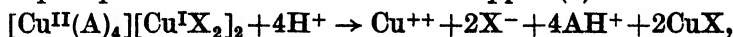
The ammonia compounds II and III readily decompose in the cold, yielding a blue solution of the tetrammine copper (II) halide and a precipitate of copper (I) halide. The ethylene diamine compounds IV and V, particularly the latter, are more insoluble than the ammonia compounds, but decompose readily on warming, yielding a purple solution of the bis-ethylene diamine copper (II) halide and a precipitate of copper (I) halide. The tetrammine dichloro compound (I) is decomposed instantly by water to form a green insoluble basic compound. The ethylene diamine compound VI yields a purple solution of the bis-ethylene diamine copper (II) chloride and a precipitate of copper (I) chloride :



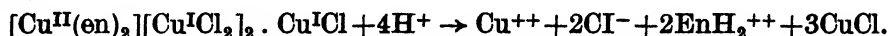
The compounds are all readily decomposed by dilute acids. With the diiodo compounds each molecule of the complex liberates an atom of iodine



with the simultaneous precipitation of copper (I) iodide, and as can be seen from the equation, each atom of iodine liberated corresponds to a molecule of divalent copper. The bromides and chlorides yield one molecule of divalent copper and a precipitate of two molecules of copper (I) halide



except with compound VI, when three molecules of copper (I) chloride are liberated :



In order to estimate the amount of divalent copper in the complexes an attempt was made to decompose the compounds with dilute acid in the presence of potassium iodide and to titrate the liberated iodine with sodium thiosulphate. With the diiodo compounds the decomposition of the ammonia compound was realized by shaking with dilute sulphuric acid containing potassium iodide. The ethylene diamine compound, being most insoluble, was decomposed by warming with dilute acetic acid containing potassium iodide. The chlorides and bromides were decomposed in oxygen-free solution saturated with hydrogen in the same

manner as compound III, and the liberated iodine in all cases was titrated with sodium thiosulphate and the addition of ammonium thiocyanate in the usual manner. The chlorides gave varying results, although of the required order to characterize the reaction. The varying results are attributed to the ease of oxidation of the copper (I) chloride in the molecule. All the titrations were performed under conditions far from ideal in that the reactions are dependent on the interaction of a solid with a liquid phase.

The highly coloured complex copper (II) cuprates (I) are insoluble in organic solvents and decomposed by water acids and alkali, particularly on heating. The ammonia compounds are more unstable than their ethylene diamine analogues and more easily oxidized in air. The order of increasing stability to oxidation is chlorides to iodides. Silver nitrate solution is immediately reduced at room temperature to metallic silver by the monovalent copper of the anion with the simultaneous precipitation of the halogen as silver halide.

No analogous pyridine complexes could be isolated by these methods due to the immediate precipitation of blue trans-planar dipyridine copper (II) chloride (Lang, 1888; Cox, Sharatt, Wardlaw and Webster, 1936) with the chloride, green dipyridine copper (II) bromide (Pfeiffer and Pimmer, 1905) with the bromide, and black hexakis—pyridine copper (II) iodide (King, 1930) with the iodide. Although the chloride and bromide are soluble in water, they are readily precipitated again on the addition of the corresponding alkali or ammonium halide, particularly on heating, and in no way could be induced to react with the complex copper (I) halides. The iodide is insoluble in water and readily loses pyridine.

The action of boiling pyridine on the ammonia or ethylene diamine compounds also did not yield the required pyridine analogues but split the complexes forming derivatives of univalent and divalent copper. The ammonia compounds yielded a complex pyridine copper (II) halide which was precipitated by the addition of benzene and which could be filtered off, whilst the benzene-pyridine filtrate on precipitation with ether deposited a white crystalline pyridine copper (I) halide soluble in benzene from which it was purified by precipitation with ether. The ethylene diamine compounds when treated similarly leave the bis-ethylene diamine copper (II) halide section of the molecule as an insoluble precipitate, whilst the filtrate yields the pyridine copper (I) halide as before. The pyridine copper (I) chloride compound was only obtained from benzene in small amounts because it is extremely rapidly oxidized to a green substance insoluble in benzene. The pyridine copper (I) halides are insoluble in water and alcohol but soluble in benzene, and readily reduce silver nitrate to the metal with simultaneous precipitation of silver halide. They probably possess the formula $[C_5H_5N \rightarrow CuX]_4^0$ and would be similar to the phosphine and arsine derivatives of silver and copper (I) iodides $[R_3P \rightarrow MI]_4^0$ and $[R_3As \rightarrow MI]_4^0$ prepared by Mann, Purdie and Wells (1936). They are not very stable and the chloride and bromide are readily oxidized in air. The order of increasing stability to oxidation is chloride to iodide. The above was established qualitatively and these pyridine copper (I) halides will be investigated further at a later date.

The preparation of a similar series of compounds $[Cu^{II}(A)_4][Cu^I XY]_2$ containing two different halogens around each copper (I) atom of the anion has been begun with the successful isolation of tetrammine copper (II) and bis-ethylene diamine copper (II) bromo-iodo-cuprates (I). Their publication is being reserved till the complete series has been investigated.

EXPERIMENTAL.

Tetrammine Copper (II) Diiodo Cuprate (I) . (III). Diammine copper (II) acetate (1.65 g. 0.0077 g. mole; Horn, 1908) in slight excess was dissolved by treating with ammonium hydroxide

(3.30 ml. of 15.0 N) followed by water (70 ml.). Added acetic acid (0.30 ml. of 17.4 N) with stirring followed by potassium iodide (20.0 g.) and when dissolved heated the solution in a water bath to 90° C. A boiling solution of copper (I) iodide (2.50 g.; 0.0131 g. mole) in water (10 ml.) containing potassium iodide (15.0 g.) was added slowly with stirring and the mixture was then cooled in ice water to 25° C. The resulting crystals were washed with 90% alcohol (25 ml.) followed by acetone (50 ml.) and air-dried as quickly as possible (tendency for compound to dissociate). This gave 4.5–4.7 g. (90–94% yield) of lustrous greenish black crystals. When the preparation was carried out at room temperature using greater quantities of potassium iodide the product was lighter in colour due to precipitation of copper (I) iodide during addition, and the ammonia content was up to 3 per cent. low. Preparations using copper sulphate in place of diammine copper (II) acetate with a smaller volume of solution and less potassium iodide gave a product contaminated with 3–5 per cent. of potassium sulphate. Hot acetone readily removes coordinated iodine and ammonia from the complex. The atmosphere above the compound in a stoppered bottle gave a blue colour with starch-iodide paper and turned red litmus paper blue, demonstrating the presence of iodine and ammonia vapours.

On heating the complex (0.3032 g.) in the oven at 105° C. to constant weight it decomposed completely to copper (I) iodide (0.2256 g.; calc., 0.2260 g.). The divalent copper in the complex was estimated from the iodine liberated by the compound on treatment with dilute sulphuric acid containing potassium iodide. The complex (1.000 g.) in a glass stoppered flask was covered with 1.5 N sulphuric acid (70 ml.) containing potassium iodide (3–5 g.). The mixture was shaken until decomposition appeared to be complete and the liberated iodine titrated with sodium thiosulphate in the usual manner, adding ammonium thiocyanate and shaking vigorously approaching the end point.

Found: Cu (total), 24.9; Cu⁺⁺, 8.17, 8.26; NH₃, 8.83; I, 66.2%.

Calculated for [Cu^{II}(NH₃)₄][Cu^II₂]₂: Cu (total), 24.89; Cu⁺⁺, 8.30; NH₃, 8.88; I, 66.25%.

Bis-ethylene Diamine Copper (II) Diiodo Cuprate (I) . (V). Anhydrous copper (II) chloride (0.82 g.; 0.0061 g. mole) was dissolved in water (25 ml.) and ethylene diamine (1.10 ml. of 69%; 0.0124 g. mole) added. Potassium iodide (5.0 g.) was then added to the stirred mixture, which was heated in a water bath to 85–90° C. To this solution was added in a fine stream with constant stirring a boiling solution of copper (I) iodide (2.33 g.; 0.0122 g. mole) in water (10 ml.) containing potassium iodide (15.0 g.). The solution containing precipitated complex was cooled in ice water with stirring to 25° C. After filtration the substance was washed with 90% alcohol (50–100 ml.) followed by acetone (50 ml.) and dried in a vacuum phosphorus pentoxide-potassium hydroxide desiccator, first removing the acetone vapours under suction. This gave 4.8 g. (96% yield) of light brown microprisms.

Owing to the compound's high insolubility the determination of liberated iodine from the divalent copper of the complex was made as follows: The complex (1.000 g.) was treated with water (20 ml.) containing acetic acid (3 ml. of 17 N) and potassium iodide (10 g.) and heated carefully till the complex had decomposed. Cooled to room temperature, added water (40 ml.) and titrated as before.

Found: Cu (total), 23.3; Cu⁺⁺, 7.80; I, 61.5%.

Calculated for [Cu^{II}(NH₂.CH₂.CH₂.NH₂)₂][Cu^II₂]₂: Cu (total), 23.30; Cu⁺⁺, 7.78; I, 62.01%.

Tetrammine Copper (II) Dibromo Cuprate (I) . (II). Anhydrous copper (II) bromide (1.93 g.; 0.0086 g. mole) was dissolved in water (25 ml.) to which was then added with stirring acetic acid (2.0 ml. of 17.4 N) followed all at once by ammonium hydroxide (4.0 ml. of 15.0 N). Potassium bromide (2.0 g.) was added and the stirred solution heated to 80° C. in a water bath and treated slowly with a hot solution (90° C.) of freshly prepared copper (I) bromide (2.48 g.; 0.0173 g. mole) in water (15.0 ml.) containing potassium bromide (10.0 g.) and two drops of 7 N hydrobromic acid. The mixture was cooled quickly in ice water to 25° C. with stirring and the filtered complex was washed with 90% alcohol (25 ml.) followed by acetone (50 ml.). The compound was dried in a vacuum desiccator as before. The reaction gave 2.2–2.7 g. (44–54% yield) of felted slate-purple prisms. The compound is readily oxidized in moist air forming basic salts.

Found: Cu (total), 32.4, 32.6; Cu⁺⁺, 11.2, 11.6; NH₃, 11.7, 11.7; Br, 54.3, 54.3, 54.7%.

Calculated for [Cu^{II}(NH₃)₄][Cu^IBr₂]₂: Cu (total), 32.98; Cu⁺⁺, 10.99; NH₃, 11.78; Br, 55.3%.

Bis-ethylene Diamine Copper (II) Dibromo Cuprate (I) . (IV). Anhydrous copper (II) bromide (1.77 g.; 0.0079 g. mole) was dissolved in water (20 ml.) and ethylene diamine (1.40 ml. of 69%; 0.0158 g. mole) followed by potassium bromide (2.0 g.) added. Heated the stirred solution in a water bath to 85–90° C. A hot solution (100° C.) of freshly prepared copper (I) bromide (2.28 g.; 0.0159 g. mole) in water (15 ml.) containing potassium bromide (10.0 g.) and two drops of 7 N hydrobromic acid was added to the above solution in a continuous stream with stirring. The solution was cooled to 25° C. in ice water and the compound filtered, washed and dried as in previous preparation. By this method obtained 2.5–3.1 g. (50–62% yield) of lustrous dark violet prisms.

Found: Cu (total), 30.3; Cu⁺⁺, 9.9, 10.1; Br, 50.5%.

Calculated for [Cu^{II}(NH₃·CH₃·CH₃·NH₃)₂][Cu^IBr₂]₂: Cu (total), 30.24; Cu⁺⁺, 10.08; Br, 50.7%.

Tetrammine Copper (II) Dichloro Cuprate (I) Monohydrate. (I). Diammine copper (II) acetate (2.69 g.; 0.0125 g. mole) was treated with ammonium hydroxide (4.0 ml. of 15.0 N) and dissolved in oxygen-free water (15 ml.) saturated with hydrogen. Ammonium chloride (2.0 g.) was added, and when dissolved, followed dropwise with stirring by acetic acid (2.0 ml. of 17.4 N). This solution was at approximately 30° C. A further solution, as follows, was prepared and added rapidly with vigorous stirring to the first solution. Freshly prepared copper (I) chloride (3.72 g.; 0.0376 g. mole) was dissolved in oxygen-free water (20 ml., saturated with hydrogen) containing ammonium chloride (10 g.) and two drops of 10 N hydrochloric acid, by warming and shaking alternately in a stoppered flask. The temperature of this last solution never exceeded 50° C. After mixing, the reaction vessel was stoppered and shaken vigorously cooling under the tap till a felted mass of crystals appeared. If crystals fail to appear it is necessary to cool by shaking in ice water. The crystals were rapidly filtered and washed with absolute alcohol (200 ml.). They were then transferred to absolute alcohol (500 ml.) in a stoppered container and thoroughly dispersed with vigorous shaking. The crystals were again filtered and washed with absolute alcohol (200 ml.) followed by chloroform (100 ml.) and the last traces of chloroform removed in a vacuum phosphorus pentoxide desiccator under suction. This gave 2.0–2.5 g. (39–48% yield) of violet prisms. The compound lost 2.7% of its weight in a phosphorus pentoxide-sodium hydroxide desiccator under vacuum (water pump) over a period of four days, and the colour changed to mauve. The colour changed similarly on heating at 70–80° C. for 45 min. and the compound (NH₃, 16.4%) lost 3.0% of its weight, which could not be accounted for by loss of ammonia (NH₃, 16.1%). The compound is rapidly oxidized in moist air and the colour changes to greenish-blue. If the compound was not thoroughly washed with absolute alcohol the ammonia and chlorine contents were extremely high due to contamination with ammonium chloride.

Found: Cu (total), 44.8, 44.9; Cu⁺⁺, 15.7, 15.9, 16.5, 17.0; NH₃, 16.44, 16.42; Cl, 34.9%.

Calculated for [Cu^{II}(NH₃)₄][Cu^ICl₂]₂·H₂O: Cu (total), 45.53; Cu⁺⁺, 15.18; NH₃, 16.27; Cl, 33.86; H₂O, 4.30%.

Bis-ethylene Diamine Copper (II) Dichloro Cuprate (I) Copper (I) Chloride . (VI). Anhydrous copper (II) chloride (1.22 g.; 0.0091 g. mole) was dissolved in oxygen-free water (25 ml.) followed by ethylene diamine (1.61 ml. of 69%; 0.0182 g. mole) and potassium chloride (2.0 g.). The mixture was then heated in a water bath to 70–75° C. whilst passing a steady stream of hydrogen. Freshly prepared copper (I) chloride (2.69 g.; 0.0272 g. mole) was dissolved in oxygen-free water (25 ml. saturated with hydrogen) containing potassium chloride (12.0 g.) and two drops of 10 N hydrochloric acid by heating to boiling, and this solution added dropwise with stirring to the previous one. The resulting mixture was cooled in ice-water to 25° C. in an atmosphere of hydrogen. The crystals were washed with 90% alcohol (50 ml.), followed by ether (50 ml.). Excess ether and moisture were removed in a phosphorus pentoxide desiccator under suction.

This gave 3.3 g. (66% yield) of purple prisms which were homogenous under the microscope. The compound is readily oxidized in air, when it assumes a blue colour.

Found: Cu (total), 46.0; Cu⁺⁺, 11.3, 12.4, 13.1; Cl, 32.3, 32.4%.

Calculated for $[\text{Cu}^{\text{II}}(\text{NH}_3 \cdot \text{CH}_3 \cdot \text{CH}_3 \cdot \text{NH}_3)_2][\text{Cu}^{\text{I}}\text{Cl}_2]_2 \cdot \text{Cu}^{\text{I}}\text{Cl}$: Cu (total), 46.08; Cu⁺⁺, 11.52; Cl, 32.15%.

The dichloro compound $[\text{Cu}^{\text{II}}(\text{NH}_3 \cdot \text{CH}_3 \cdot \text{CH}_3 \cdot \text{NH}_3)_2][\text{Cu}^{\text{I}}\text{Cl}_2]_2$ would require Cu (total), 42.13; Cu⁺⁺, 14.04; Cl, 31.32%.

SUMMARY.

The reaction of one mole of tetrammine and bis-ethylene diamine copper (II) halides with two moles of the corresponding copper (I) halide dissolved in a concentrated solution of alkali halide has been found to yield highly coloured crystalline tetrammine copper (II) dihalogen cuprates (I) $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{X}_2]_2$. The bis-ethylene diamine copper (II) dichloro cuprate (I) could not be prepared but a compound $[\text{Cu}^{\text{II}}(\text{en})_2][\text{Cu}^{\text{I}}_3\text{Cl}_5]$ was obtained if the mole ratio of bis-ethylene diamine copper (II) chloride to copper (I) chloride was 1:2 or 1:3. It is suggested that the extra molecule of copper (I) chloride is involved in the crystal lattice of the compound and that the ion $[\text{Cu}^{\text{I}}_3\text{Cl}_5]^{--}$ has no existence, but rather the compound is more correctly represented as $[\text{Cu}^{\text{II}}(\text{en})_2][\text{Cu}^{\text{I}}\text{Cl}_2]_2 \cdot \text{Cu}^{\text{I}}\text{Cl}$. The reactions of these compounds have been studied. An attempt to prepare a similar series with pyridine was unsuccessful.

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MAGNETIC PROPERTIES OF SOME TUNGSTEN BRONZES.

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Tungsten "bronzes" are not, as the name implies, alloys, but non-stoichiometric compounds with the general formula R_xWO_3 , where R is an alkali metal and x lies between 0 and 1. The bronzes possess striking colours, ranging from yellow through reddish brown to blue, which are no doubt due in some way to the fact that they contain both W^v and W^{vi} . Hagg (1935) has correlated the composition with colour, unit cell dimension and density of the sodium bronzes; as x becomes smaller, that is, as more and more sodium ions are missing from the lattice, the cell dimension decreases and the colour changes from yellow to blue. In their optical properties the bronzes resemble the metals (Hagg, 1935). Nothing appears to be known of their magnetic properties (Selwood, 1943). An investigation of these properties was therefore undertaken in the hope of throwing further light on the constitution of the bronzes.

Since W^v contains one unpaired electron and W^{vi} none, it seemed probable that a knowledge of the magnetic moment* of a bronze might enable the calculation of the proportion of W^v to W^{vi} which could then be checked against chemical analysis.

Preliminary measurements of susceptibilities at room temperatures showed that there was no agreement between the values of x calculated from magnetic data using the relationship $\mu = 2.83\sqrt{\psi MT}$ and those found from chemical analysis. The magnetic method of calculating x is of course based on the assumption that the magnetic susceptibility is temperature dependent and follows the simple Curie Law ($\psi = C/T$). Because of the disagreement between the two values of x an attempt was made to discover whether the susceptibilities of the bronzes followed the Curie-Weiss Law ($\psi = C/T + \Delta$) or whether they were not independent of temperature altogether. Over the range of temperature studied (290–480° K.) it was found that, within the limits of experimental error, susceptibilities were in fact temperature independent.

EXPERIMENTAL.

Several sodium and potassium tungsten bronzes were made by fusing tungstic acid and alkali carbonate in different proportions and reducing the powdered fusion product by heating at a red heat under a stream of coal gas for several hours (Phillipp, 1882). The resulting bronze was then treated successively with boiling water, potassium hydroxide solution, hydrochloric acid, aqua regia, potassium hydroxide solution and finally water. When examined under the microscope the preparations appeared to be homogeneous. The products were analysed by using the method of Schaefer (1904). Several sodium bronzes were also examined by X-ray powder diffraction methods. (Hagg, 1935) and except in one instance there was reasonable agreement between the values of x derived by the chemical and X-ray methods. In that one case the X-ray value of x was adopted.

* Magnetic moment, μ of an atom (in Bohr magnetons) is related to the number of unpaired electrons (n) it contains by the formula $\mu = \sqrt{n(n+2)}$.

Magnetic measurements were made by means of the Gouy method using an analytical balance sensitive to 0.1 mgm. Tubes were calibrated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ assumed to have a susceptibility 5.92×10^{-8} at 19°C . (Mellor, 1943). The diamagnetic corrections used were those quoted by Van Vleck (1932). Measured susceptibilities were usually so small that they were of the same order as the diamagnetic corrections. No great accuracy can therefore be claimed for moments derived from these measurements.

RESULTS.

Some typical measurements at room temperature are shown in Table I.

TABLE I.

Specimen.	$\psi \times 10^6$	M.W.	$\psi_M \times 10^6$	Dia- magnetic Correc- tion.	$\psi_A \times 10^6$	μ_{eff} Bohr Magnetons.
Sodium bronze—						
I	0.20	248.0	50	40.7	90	0.46
II	0.43	251.6	110	41.3	150	0.59
III	0.42	252.7	110	41.6	150	0.59
Potassium bronze—						
I	0.20	256.6	50	48.7	100	0.48
II	0.13	254.3	30	47.3	80	0.44
III	0.22	261.7	60	50.5	110	0.52

On the assumption that μ_{eff} for one unpaired electron spin is $1.73\mu_B$ * the above values were used to calculate the proportion of W^∇ in each specimen and thereby the value of x .

From Table II it is clear that "spin only" theory which accounts so satisfactorily for the moments of many transition elements is not applicable to the

TABLE II.

Specimen.	μ_{eff} (obs.)	x from Magnetic Data.	x from Chemical and X-ray Analysis.	Predicted Value of μ_{eff} Calculated from x .
Sodium bronze I	0.46	0.10	0.6-0.7	1.38
Sodium bronze II	0.59	0.16	0.92	1.64
Potassium bronze I	0.48	0.09	0.63	1.29
Potassium bronze II	0.44	0.09	0.57	1.21

tungsten bronzes. The moments in these substances are much smaller than required by this theory.

Measurements on several bronzes were next made over a range of temperatures (292 – 485°K). Specimens were heated in a small, tubular, non-inductively

* This is the theoretical value. Few experimental values for the moment of W^∇ are available but those reported are lower (1.53). Adoption of this lower value would not affect the conclusion of the present paper.

wound electric furnace mounted between the pole pieces. Although the furnace was made as small as possible, the pole pieces had to be moved further apart than in the previous experiments. The consequent weakening of the field further reduced the accuracy of measurements. The results for two bronzes are summarized in Table III.

TABLE III.

The Magnetic Susceptibility of Some Tungsten Bronzes at Different Temperatures.

Specimen.	Temperature. (° K.)	Magnetic Susceptibility. ($\times 10^6$.)
Sodium bronze III ($\text{Na}_{0.8}\text{WO}_3$) ..	292	0.45 ± 0.03
	400	0.45 ± 0.04
	419	0.43 ± 0.03
	430	0.41 ± 0.03
	443	0.42 ± 0.03
	452	0.40 ± 0.04
	456	0.41 ± 0.03
	461	0.43 ± 0.03
	469	0.40 ± 0.03
	482	0.35 ± 0.07
	485	0.33 ± 0.07
Potassium bronze II ($\text{K}_{0.8}\text{WO}_3$)..	300	0.15 ± 0.04
	415	0.12 ± 0.04
	432	0.10 ± 0.04
	444	0.14 ± 0.04
	455	0.14 ± 0.04
	457	0.13 ± 0.04

From Table III it is evident that over the limited temperature range studied susceptibility is independent of temperature within the limits of experimental error.

This temperature-independent paramagnetism is consistent with the view that the tungsten bronzes contain quasi-metallic electrons.* Pauli's (1927) explanation of the temperature independent paramagnetic susceptibility of metals is applicable here. All electrons not in closed shells are partly free to move in permitted energy zones in the solid and to pair with electrons from other atoms. As the temperature increases, the number of unpaired electrons is increased, many electrons having been raised to higher energy levels. The number of unpaired electrons at the lower temperatures is smaller than it would be if the electrons were firmly bound, thus accounting for the low value of the observed moments. However, the increase in temperature also results in an increasing tendency to random orientation of unpaired spins. The two effects approximately cancel each other, so that paramagnetic susceptibility due to partially free electrons is roughly temperature-independent.

SUMMARY.

Tungsten bronzes show a small paramagnetic susceptibility which is roughly temperature-independent—at least in the range 290–470° K. This susceptibility is due to partially free electrons and is consistent with the view that the tungsten bronzes are semi-conductors.

* Tungsten bronzes show the marked increase in electric conductivity with increasing temperature which is characteristic of semiconductors. Thermo-electromotive force measurements show that the bronzes are electron conductors (private communication from Dr. J. S. Anderson, Chemistry Department, University of Melbourne).

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DISPROPORTIONATION EQUILIBRIA IN ALKALINE EARTH IONS.

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INTRODUCTION.

Experimental work on disproportionation equilibria in inorganic systems is very meagre. On the other hand, the study of these equilibria in organic systems is comparatively advanced, due in large part to the investigations of Michaelis and his co-workers. The advances in the organic field have all followed upon the discovery (made independently by Michaelis and Elema (1931)) that analysis of the potentiometric titration curves of many reversible organic redox systems involving the overall transfer of more than one electron shows the presence in solution of compounds of oxidation state intermediate between the oxidation states of oxidant and reductant, and in thermodynamic equilibrium with these species, i.e. of semiquinones. When this was established, the problem of assigning structures to compounds isolated from such mixtures, the empirical formulæ of which could not be reconciled with classical valence concepts, was largely solved: they were shown to be either monomeric or dimeric semiquinones.

The absence of similar advances in the inorganic field is due to the fact that there are very few inorganic redox systems involving disproportionation which can be studied in this comparatively straightforward way. The reason for this is also the reason why semiquinone radicals have not been detected until recently—viz. that the potentiometric method is relatively insensitive, and intermediate formation can be detected by means of it only when the disproportionation constant (equilibrium constant of the reaction $2(\text{Int.}) \rightleftharpoons (\text{Ox.}) + (\text{Red.})$) is less than 10^2 . The disproportionation constants in simple inorganic systems are in general either much larger than 10^2 or so much smaller that one ion of limiting state exists only in minute amount in equilibrium with the intermediate and the other ion: hence ions to "anomalous" valence states commonly escape detection in multivalent redox reactions. Other methods must, in general, be employed to detect such ions. The discovery of the Sn^{3+} ion in aqueous solution in equilibrium with Sn^{2+} and Sn^{4+} was made by Ball, Wulfkuehler and Wingard (1935) by the use of magneto-optical techniques, and the discovery of Cd^+ and Zn^+ as intermediates in the reduction in aqueous solution of the divalent ions was made by Prytz and Østerud (1942) and Heyrovsky (1947) by the use of ingenious polarographic methods.

While it must be recognized that present knowledge of disproportionation equilibria in inorganic systems is fragmentary, the principles of such equilibria established by the study of organic redox systems provide a guide to investigation in this field. One fact in particular that is illustrated by the discovery of semiquinones and which is true for any system, organic or inorganic, must be emphasized: it is that whenever an ion, element or molecule of oxidation state x is in thermodynamic equilibrium with an ion in solution of oxidation state $x+n$, there exist also in solution ions of all oxidation states from $x+(n-1)$

to $x+1$ where n is positive, or from $x+(n+1)$ to $x-1$ where n is negative, in disproportionation equilibrium with these species. The validity of this is seen when it is realized that to deny it is, in the case of inorganic ionic systems, to assert that there is in some cases an infinite difference of free energy between aqueous ions of the same element but of different oxidation states.

This immediately rules out such confused notions as Kirk and Browne's (1928) concept (independently suggested by Shaffer (1933)) of "didelectronators", i.e. molecules or ions which can accept from reductants no less than two electrons. In spite of this, however, the possibility of some ions acting as pure "didelectronators" is still being investigated by Remick (1947). It is symptomatic of the unsatisfactory state of disproportionation theory that this error is repeated by Wilson and Bremner (1948) in the only comprehensive review of inorganic disproportionation equilibria yet published. These authors remark (*op. cit.*, p. 2): "If we consider the reaction when a biavalent metal is oxidized to a salt $M-2e=M^{2+}$, a bivalent oxidation, we can see that if the metal has only one state of valency, e.g. magnesium, the reaction cannot proceed in any other way—there are no univalent compounds of magnesium." (Presumably this is also considered to be true of all the alkaline earths, since no equilibria involving $+1$ ions of any metal of this group is discussed by these authors.) Apart from the general issues (the most important of which is the suggestion that the existence of ions of intermediate valence states in *compounds* of an element is a criterion of the existence of these ions in solution) a more unfortunate example could scarcely have been chosen: for of all the alkaline earth metals, magnesium is the one of which the greatest number of compounds containing the metal in oxidation state $+1$ is known, the most important of these being the Grignard reagents.

In this paper, the evidence for the existence of disproportionation equilibria involving alkaline earth ions of oxidation state $+1$ in the vapour, liquid and solid states, and in aqueous and non-aqueous solution, is discussed. It is shown that the lack of general recognition of the existence of these equilibria is inconsistent with experiment. The existence of these equilibria in a group of elements in which this might be thought to be unlikely (all the commoner compounds of the alkaline earths containing the ions of oxidation state $+2$) is a confirmation of the view that disproportionation equilibria are at least as widespread and of equal importance in the inorganic as in the organic field.

THE M/M^+ POTENTIALS IN AQUEOUS SOLUTION AND THE DISPROPORTIONATION EQUILIBRIUM.

The theoretical calculation of intermediate potentials has not hitherto been attempted. In a recent publication,* however, it was shown that the free energy of formation of an aqueous ion (ΔF_f°) may be calculated when the free energy of sublimation (ΔF_s°) and ionization (ΔF_i°) of the element, and the real free energy of hydration of the ion (ΔF_h°) are known, according to Eq. 1.

$$\Delta F_f^\circ = \Delta F_s^\circ + \Delta F_i^\circ + \Delta F_h^\circ - z(103.92) \text{ Kcal.} \dots\dots\dots (1)$$

In the same publication it was shown that the real free energy of hydration of cations of noble gas structure may be accurately calculated by means of the modified Born equation 2,

* Hush (1948).

$$-\Delta F_h^\circ = \frac{Nz^2e^2}{2(r_c + 0.86)} (1 - 1/D) + 6.9z \text{ Kcal.} \dots\dots\dots (2)$$

where z is the valency and r_c the Pauling crystal radius of the ion.†

The application of Eq. (2) is in general restricted to ions of noble gas structure since it has been assumed, in deriving the equation, that the hydration energy is entirely electrostatic in nature; this will be the case only when the polarizability of the ion is small in comparison with the crystal radius (as in ions of this kind), entailing that the van der Waals potential of the ion is small and of the same order as that of the substituted water molecules. Within the accuracy of these calculations, this may also be assumed true of univalent ions of the alkaline earth elements. The crystal radii of the univalent ions are of course not directly known, but they have been estimated from the radii of the divalent ions by means of the relationship $r_c(M^+) = r_c(M^{2+}) + 0.16 \text{ \AA}$. The real free energies of hydration of the univalent alkaline earth metals, on these assumptions, are as shown in Table I.

TABLE I.

Real Free Energy of Hydration of Univalent Gaseous Alkaline Earth Ions.

Ion.				r_c (\AA .)	$-\Delta F_h^\circ$ (Kcal.)
Be ⁺	1.33	129.3
Mg ⁺	1.67	104.4
Ca ⁺	2.01	87.9
Sr ⁺	2.15	82.6
Ba ⁺	2.37	76.6

With the values of ΔF_h° thus calculated, the potentials M/M^+ may be evaluated according to Eq. (1). This calculation is shown in Table II. The potentials M^+/M^{2+} , which have been calculated from the relationship $E(M^+/M^{2+}) = 2E(M/M^{2+}) - E(M/M^+)$, are also included.

TABLE II.

Normal Potentials M/M^+ and M^+/M^{2+} of the Alkaline Earth Metals.

Metal.		$-\Delta F_h^\circ$ (Kcal.)	ΔF_1° (Kcal.)	ΔF_s° (Kcal.)	ΔF_f° (Kcal.)	$E_0(M/M^+)$ (v.)	$E_0(M/M^{2+})$ (v.)	$E_0(M^+/M^{2+})$ (v.)
Be	..	129.3	214.0	66.0	46.8	+2.1	-1.7	-5.5
Mg	..	104.4	175.6	27.6	-4.3	-0.2	-2.3	-4.4
Ca	..	87.9	140.5	34.5	-17.0	-0.7	-2.9	-5.1
Sr	..	82.6	130.8	30.7	-25.0	-1.1	-2.9	-4.7
Ba	..	76.6	119.8	41.4	-19.3	-0.8	-2.9	-5.0

† An example will be given to illustrate the accuracy of this method. The ion Sr^{2+} has a noble gas structure, hence the potential Sr/Sr^{2+} may be calculated according to Eqs. (1) and (2), given the values of r_c , ΔF_s° and ΔF_1° . The value of r_c is 1.13 \AA .; thus according to Eq. 2, ΔF_h° is -341.1 Kcal. Substituting in Eq. 1, using the known values of ΔF_1° and F_s° , we obtain $-\Delta F_f^\circ = -385.51 - 30.70 + 341.1 + 207.84 = 132.7 \text{ Kcal}$. The calculated Sr/Sr^{2+} potential is thus -2.88 v. on the absolute hydrogen scale, as compared with the experimental value of -2.90 v. In general, an accuracy of the order of ± 0.1 v. is to be expected in the theoretical calculation of potentials.

It is evident that the normal potentials for the two one-electron steps of the oxidation of alkaline earth metals to oxidation state +2 or reduction of the divalent ions to oxidation state 0 are in inverse order, and so widely separated that the disproportionation equilibrium in aqueous solution $2M^{+} \rightleftharpoons M + M^{2+}$ lies far to the right. The constant for this equilibrium in each of the systems may be calculated from the potential data of Table II, since the free energy of disproportionation (ΔF_d) is given by

$$\Delta F_d^{\circ} = \Delta F_r^{\circ}(M^{2+}) - 2 \Delta F_r^{\circ}(M^{+})$$

The values of ΔF_d° and the equilibrium constant in each case are shown in Table III.

TABLE III.

The Free Energy of Disproportionation of Aqueous M^{+} Ions.

Metal.	$-\Delta F_d^{\circ}$ (Kcal.)	Log K_d .
Be	172	126
Mg	99	73
Ca	99	73
Sr	83	61
Ba	98	72

From the high values of K_d for each of these systems, it may be inferred that (monomeric) salts of +1 ions of the alkaline earths cannot be isolated from aqueous solution. In order to isolate such salts, it would be necessary that the ratio of the solubility product of the divalent compound to that of the monovalent compound, in the case of salts with a divalent anion (and that the ratio of the solubility product of the divalent compound to the square of that of the monovalent compound, in the case of salts with a monovalent anion) be 10^{126} for Be salts and of the order of 10^{70} for the remaining alkaline earth salts. It is evident, however, that this is highly unlikely; it can be calculated that in the case of halides, assuming* the lattice energies of the +1 salts to be approximately those of the corresponding alkali halides, the ratio does not differ significantly from 1.†

The high value of K_d for these systems would also be expected to affect the kinetics of reactions in which aqueous +2 ions are reduced to the metal, or the metal is oxidized to aqueous +2 ions. The only published data which is relevant to this appears to be that on the rate of solution of the alkaline earth metals in water and acids, and although these reactions are too complex to be discussed in any detail here, it may not be coincidental that those metals of the alkaline earth group which are not oxidized by hydrogen ion in pure water at room temperature (viz. Be and Mg) even though the M/M^{2+} potentials are in each case sufficiently low to make this thermodynamically possible, are also the metals for which the potential of the first step of reduction is higher than that of the hydrogen/hydrogen ion couple at pH 7 (-0.41 v.). ‡

* The approximate correctness of this assumption is shown in the next section.

† This calculation makes use of the hydration energies derived above for the monovalent ions and those already published (Hush, *op. cit.*) for the divalent ions and the halide ions.

‡ The connection between high value of dismutation constant and sluggishness of reaction has been discussed by Michaelis (1937).

No account has been paid so far to the possibility of dimerization of the aqueous M^+ ions by pairing of the 3s electrons, although this probably occurs. Such dimerization, if it occurs, will of course not affect the above derivation of intermediate potentials, but will nevertheless result in increased stability of the +1 form. No calculations of the dimerization equilibria can be made, but even if dimerization is practically complete it cannot be expected that solid salts containing dimerized M^+ ions will be isolated from aqueous solution. Such salts would only be isolated if the values of ΔF for the reaction $2M^+ \rightarrow (M^+)_2$ were of the order of -100 to -170 Kcal., and this is most unlikely.

ALKALINE EARTH SUBHALIDES IN THE VAPOUR AND CRYSTALLINE STATES :
HEATS OF FORMATION, DISPROPORTIONATION AND DIMERIZATION.

The existence of alkaline earth subhalides, in which the metal is in oxidation state +1, has been debated, but in fact sufficient data are available to make possible the deciding of this issue.

There is no doubt that halides of formula MX exist in the vapour state at *ca.* 1000°C . in equilibrium with the metal and the divalent compounds. The absorption spectra of alkaline earth halides in the visible and ultra-violet were examined by Walters and Barratt (1928), and bands were identified as being due to the presence of each halide (F, Cl, Br and I) of Mg, Sr, Ca and Ba. These were shown to be not dimers of formula M_2X_2 , but monomers of formula MX . Johnson (1929) examined the band spectra of MgF , CaF and BaF in the vapour state and deduced the energy of dissociation of CaF into gaseous atoms. Parker (1935) published a vibrational analysis of band systems due to $MgCl$, $CaCl$ and $SrCl$ vapour.*

Crystalline products of reaction between normal alkaline earth halides and the metal at high temperature, of empirical formula MX , have long been known. A crystalline product of empirical formula $CaCl$ was obtained during electrolysis of fused $CaCl_2$ by Borchers and Stockem (1902, 1903) and Danneel and Stockem (1905). This product was obtained by Wöhler and Rodewald (1909) by heating metallic Ca with $CaCl_2$ in equivalent proportions at 900 – 1000°C . in a steel cylinder, and by Benoit and Guntz (1924) in a similar fashion. Crystalline products of empirical formulæ CaF and CaI were obtained by Wöhler and Rodewald (1909) by the same method as used in the preparation of $CaCl$, the temperatures being 1400°C . and 800°C . respectively. A double salt $NaF.BaF$ was obtained by Guntz (1902), by heating NaF with BaF_2 at 800°C . An almost theoretical yield of a crystalline product of empirical formula $BaCl$ was obtained by Haber and Tolloczko (1904) and by Haber (1908) by the electrolysis of fused $BaCl_2$ in a nitrogen atmosphere at 600°C . The same product was obtained by Benoit and Guntz (1924) by heating metallic barium with $BaCl_2$ at high temperature. These authors also prepared $BaBr$, BaF and BaI . A double compound of BaF with NaF was described by Guntz (1902). Benoit and Guntz also obtained $SrCl$, $SrBr$, SrF and SrI by their usual method.

The facts which appear to be decisive in favour of the view that these compounds are actually subhalides, and not mixtures or solid solutions of the metal and the dichloride are the following :

(i) The salts retain their characteristic properties after precautions have been taken to remove excess metal and dichloride. Thus Wöhler and Rodewald purified their compounds by suspending the salts first in ethyl iodide, thus precipitating any excess metal, and then in bromoform, thus separating excess dichloride.

* The spectrum of MgF has also been investigated by Jenkins and Grinfeld (1933, 1934) and (together with that of BeF) by Jevons (1929).

(ii) The colours, streaks and lustres of the salts are those characteristic of compounds of unstable valence type, and could not be accounted for on the mixture or solid solution hypotheses. Calcium subchloride, according to both Wöhler and Rodewald (1909) and Borchers and Stockem (1902) form bright red to violet pleochroic crystals. Calcium subfluoride and calcium subiodide form (according to Wöhler and Rodewald) respectively red-orange and brown crystals, the subfluoride having a metallic lustre. The strontium and barium subhalides, according to Benoit and Guntz (1924) are all deep brown, the barium salts having a violet streak.

(iii) The heat of interaction of the metal and the metal chloride to form MX may be calculated from the data of Benoit and Guntz on the heat of solution of the subchlorides in acid. These are (at least in the case of Ba and Sr) of the order of $-\Delta H = 16$ Kcal. for the reactions of $M + MX_2 \rightarrow 2MX$, which are larger than could be expected for the formation of a solid solution.

Taking it that the salts are subhalides, containing the metal in oxidation state +1, the question may now be asked whether these salts are simple monomers of formula MX, or dimers, or perhaps higher polymers. This may be approached in the following manner. Since the heats of formulation of gaseous M^+ and X^- are known, the heat of formation of $MX(c)$ could be calculated by means of a Born-Haber cycle if the lattice energy of MX were known. If the salt is a monomer, one may assume the lattice energy to be that of the corresponding alkali halide, with tolerable accuracy and thus the heat of formation may be approximated: this will actually lead to a slightly high value of $-\Delta H_f^\circ(c)$, since the alkaline earth ions have larger radii. For the sub-fluorides, these values may be checked by an independent calculation, employing the data of Johnson (1929) for the heats of dissociation into gaseous atoms, assuming that the heats of sublimation of the subfluorides are approximately the same as those of the corresponding alkali fluorides. From the heat of formation, one may calculate the heat of the disproportionation reaction $MX \rightarrow \frac{1}{2}M + \frac{1}{2}MX_2$. These calculations for Mg, Sr and Ca are shown in Table IV.

The approximate agreement of the values of $\Delta H_f^\circ(c)$ calculated independently for CaF and SrF by methods (a) and (b) is good evidence that these figures are of the correct order of magnitude—i.e. that the reaction $M(c) + \frac{1}{2}X_2(g) \rightarrow MX(c)$ is exothermic to the extent of about 60 Kcal. It may be assumed that the entropy changes in these reactions are small,* so that the heats and free energies of reaction may be assumed to be of approximately the same order of magnitude. It is then seen that, in spite of the large negative value of $\Delta H_f^\circ(c)$, the heat of disproportionation is so large that subfluorides of these alkaline earth metals of formula MX are so unstable with respect to the decomposition $MX(c) \rightarrow \frac{1}{2}M(c) + \frac{1}{2}MX_2(c)$ that it is impossible that a crystalline monomeric subfluoride could be isolated. Calculations of ΔH_d° for other subhalides of alkaline earth metals by the same method as employed in Table IV have been made by Grimm and Herzfeld (1923); the values are in every case of the same order of magnitude as those of the subfluorides, and it is thus possible to generalize, and to assert that *no crystalline alkaline earth subhalide has the simple monomeric formula MX*.

The most probable alternative is that the subhalides contain $(M-M)^{2+}$ ions, formed by pairing of the lone 3s electrons (cf. mercurous halides), and are thus dimeric, represented by the formula $(M^+)_2X_2$. The energy relationships on this view may be worked out from the data of Benoit and Guntz (1924) on the heats of solution of the subchlorides of Ba, Sr and Ca in dilute acid. The net process

* Cf. Latimer (1938).

TABLE IV.

Approximate Theoretical Heats of Formation and Disproportionation of Monomeric Alkaline Earth Subfluorides.

Salt.	$\Delta H_f^\circ(\text{g})$ (Kcal.)	ΔH_s° (Kcal.)	$\Delta H_f^\circ(\text{c})$ (Kcal.)		ΔH_d° (Kcal.)
			(a)	(b)	
MgF ..	—	72	—	—68	—64
CaF ..	3	50	—47	—69	—76
SrF ..	2	53	—51	—71	—74

$\Delta H_f^\circ(\text{g})$: heat of the reaction $\text{M}(\text{c}) + \frac{1}{2}\text{X}_2(\text{g}) \rightarrow \text{MX}(\text{g})$, from data of Johnson.*

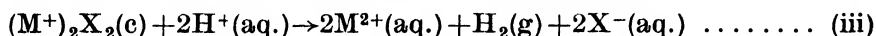
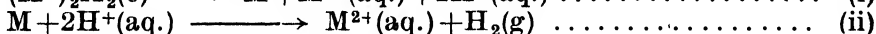
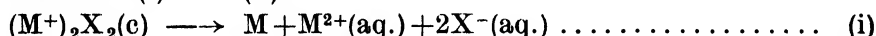
ΔH_s° : heat of sublimation of $\text{MX}(\text{c})$, assumed to be equal to the heat of sublimation of the corresponding alkali fluoride.

$\Delta H_f^\circ(\text{c})$: heat of the reaction $\text{M}(\text{c}) + \frac{1}{2}\text{X}_2(\text{g}) \rightarrow \text{MX}(\text{c})$; (a) calculated from $\Delta H_f^\circ(\text{g})$ and ΔH_s° , (b) calculated by means of a Born-Haber cycle, assuming the lattice energies of the subfluorides to be those of the corresponding alkali fluorides.

ΔH_d° : heat of the disproportionation reaction $\text{MX}(\text{c}) \rightarrow \frac{1}{2}\text{M}(\text{c}) + \frac{1}{2}\text{MX}_2(\text{c})$ calculated from $\Delta H_f^\circ(\text{c})$ derived by method (b) and the heat of formation of $\text{MX}_2(\text{c})$.

* There appears to be some confusion in the derivation of $\Delta H_f^\circ(\text{g})$ values for SrF and MgF by Bichowsky and Rossini (1936) which has misled later investigators (e.g. Latimer, 1938). In the text, Bichowsky and Rossini state that Johnson (1929) gave values for the energy of dissociation (D) of MgF, CaF and SrF into gaseous atoms. In the table, the only value of D shown is for SrF, given as 77 Kcal. The heats of formation of MgF, CaF and SrF are given in the table as 95, 3 and 27 Kcal. In the reference cited, however, Johnson reports only one value of D, viz. that of CaF; this is given as 77.46 Kcal. (assuming the Ca atom to be in the 2^3P state). It is remarked that the dissociation energy of SrF is probably of the same order as this, and in the calculation of $\Delta H_f^\circ(\text{g})$ in Table IV it has been assumed to be the same. The value of D for MgF is not discussed by Johnson. The value of D for CaF cited gives (together with the heats of sublimation of Ca(c) and dissociation of $\text{F}_2(\text{g})$) $\Delta H = 3$ for the reaction $\text{Ca}(\text{c}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{CaF}(\text{g})$. Assuming as a first approximation that D for SrF is also 77 Kcal., we calculate for $\text{Sr}(\text{c}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{SrF}(\text{g})$ $\Delta H = 2$ Kcal. This latter value is in marked disagreement with that given by Bichowsky and Rossini. Since D for MgF has not been estimated, the heat of formation of gaseous MgF cannot be calculated in this manner.

of solution is represented by Eq. (iii) below; this may be regarded as the sum of the two reactions (i) and (ii):



Since the heats of reactions (ii) and (iii) are known, that of (i) may be calculated, and from this the heat of formation and disproportionation of $(\text{M}^+)_2\text{X}_2(\text{c})$ evaluated in the usual way. The heat of dimerization may be evaluated with fair accuracy by estimating the heat of formation of the monomer $\text{MX}(\text{c})$ by the same method as employed in calculating $\Delta H_f^\circ(\text{c})$ for the subfluorides in Table IV (in which a monomeric structure was assumed) and combining this with the actual heat of formation of the dimer. The values so obtained are shown in Table V.

From the data of Table V, it is evident that each subhalide, viewed as the dimer $(\text{M}^+)_2\text{X}_2$, has a large negative heat of formation, and that all are stable (although $(\text{Ca}^+)_2\text{Cl}_2$ is less so than the other two salts) to disproportionation. This is sufficient to account for the existence of the subhalides as fairly stable salts at ordinary temperature. This entails that the lattice energies of the subhalides approach the order of magnitude of those of the normal dihalides. The actual energies cannot be calculated exactly, since the heats of the reactions $2\text{M}^+(\text{g}) \rightarrow (\text{M}^+)_2(\text{g})$ are not known. Assuming that these have approximately

the same value in each case, and that this is of the order of magnitude of the heat of dimerization of gaseous alkali metal atoms, we may set ΔH for the above reaction very roughly at -10 Kcal. On this assumption, the lattice energies of $(\text{Ba}^+)_2\text{Cl}_2$, $(\text{Sr}^+)_2\text{Cl}_2$ and $(\text{Ca}^+)_2\text{Cl}_2$ respectively (calculated from a Born-Haber cycle) are 430, 460 and 460 Kcal. Comparison with the lattice energies of the corresponding dichlorides (474, 501 and 532 Kcal.) shows that, as would be expected, the lattice energies of the subchlorides are smaller than but of the same order as those of the dichlorides.

TABLE V.

Heats of Reaction of Subchlorides of Ba, Sr and Ca.

Metal	$\Delta H_f^\circ(\text{c})$ Calculated for Monomer. (Kcal.)	$\Delta H_f^\circ(\text{c})$ Calculated for Dimer. (Kcal.)	ΔH_d° Calculated for Dimer and Monomer. (Kcal.)	ΔH_d° Calculated for Dimer. (Kcal.)
Ba	-55.9	-222.4	-110.6	17.0
Sr	-42.2	-213.2	-128.8	15.2
Ca	-35.7	-194.0	-122.6	3.4

$\Delta H_f^\circ(\text{c})$, calculated for monomer: Heat of the reaction $\text{M}_c + \frac{1}{2}\text{X}_2(\text{g}) \rightarrow \text{MX}(\text{c})$ calculated theoretically by means of a Born-Haber cycle, assuming the lattice energies of the monomeric subchlorides to be the same as those of the corresponding alkali chlorides.

$\Delta H_f^\circ(\text{c})$, calculated for dimer: Heat of the reaction $2\text{M}(\text{c}) + \text{X}_2(\text{g}) \rightarrow (\text{M}^+)_2\text{X}_2(\text{c})$ calculated from the data of Benoit and Guntz (1924) on heats of solution, and heat of formation of M^{2+} (aq.).

ΔH_d° : Heat of dimerization of $\text{MX}(\text{c})$, i.e. heat of the reaction $2\text{MX}(\text{c}) \rightarrow (\text{M}^+)_2\text{X}_2(\text{c})$, calculated from $\Delta H_f^\circ(\text{c})$ values for monomer and dimer.

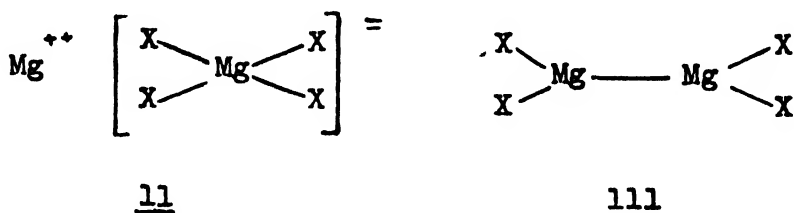
ΔH_d° : Heat of the disproportionation reaction $(\text{M}^+)_2\text{X}_2(\text{c}) \rightarrow \text{M}(\text{c}) + \text{MX}_2(\text{c})$ calculated from $\Delta H_f^\circ(\text{c})$ and heat of formation of $\text{MX}_2(\text{c})$.

One important result of the positive values of heats of disproportionation of the solid subchlorides shown in Table V is the difficulty of electrolytic reduction of the dichlorides to the metal. This is so marked that, as has been pointed out above, electrolysis of the dichlorides has served as a preparative method for obtaining the solid subchlorides. Benoit and Guntz (*op. cit.*) found that barium could not be obtained by the electrolysis of barium chloride under any conditions, and that only a minute amount of strontium was obtained by electrolysis of strontium chloride, although in both cases the subchlorides were formed. A higher yield of the subchloride of barium from electrolysis was claimed by Haber and Tolloczko (*op. cit.*) who calculated from their potential data a value of 34.6 Kcal. for ΔH_d at 600°C ., which is of the same sign as the value found for the reaction at 25°C . in Table V, and of an order of magnitude in reasonable agreement with it, the temperature effect being taken into account.

ORGANOMAGNESIUM HALIDES.

The formation of compounds of empirical formula RMgX (Grignard reagents), where R is an alkyl or aryl radical and X a halogen, by reacting metallic magnesium with the organic halide is well known. The reaction usually goes to completion in dry ether; it may also be carried out in toluene, benzene, xylene, petroleum ether and tertiary amines (Tschelinzeff, 1904) or in the complete absence of solvent (Lohr, 1891; Shorugin and Isagulyantz, 1936). From each solvent, products RMgX may be isolated as crystalline solids, either solvent-free or, when the solvent molecule contains available co-ordination pairs, solvated.

There has been much controversy over the structure of Grignard reagents, and the problem has not been systematically investigated. The simple structure RMgX (I), in disproportionation equilibrium with R_2Mg and MgX_2 , was proposed by Schlenk and Schlenk in 1929. The main alternative formulæ that have been discussed are those of Terentiev (1926), who proposed the ionic complex II, and Jolibois, who proposed the "loose complex" III for the non-solvated species.



The issues here are :

- (i) Does a solution or a crystalline precipitate of a Grignard reagent contain a species $(\text{RMgX})_n$ (i.e. either I, II or III) in equilibrium with the species MgX_2 and MgR_2 ?
- (ii) If there is such an equilibrium, is the Mg in the first species in oxidation state +1?
- (iii) If there is a species $(\text{RMgX})_n$, is n equal to 1 or 2?

Discussion of these issues will be confined to the properties of Grignard reagents in solution, since little is known about the properties of the solid compounds. The first point may be answered definitely. Schlenk and Schlenk (1926) were able to isolate quantitatively $(\text{RMgX})_n$ and MgX_2 from solutions of Grignard reagents by dioxane precipitation, leaving in solution R_2Mg , and by this method the position of equilibrium in many Grignard solutions was determined. A phenomenon which Schlenk and Schlenk were unable to explain—viz. that all Grignard solutions on continued standing slowly deposit MgX_2 —was investigated more recently by Noller and Raney (1940). These authors propose new values for the equilibrium constants, but confirm the existence of the equilibrium in solution. The effect of various solvents on the equilibrium has been studied by Miller and Bachmann (1935). It may thus be assumed that the equilibrium exists.

The second point cannot be answered so definitely, since it is not easy to see what could conclusively distinguish a species of oxidation state +1 from the other alternatives, but all the evidence is consistent with the view that the magnesium is in this state. A large number of electrolysis studies have been made of Grignard reagents in ether solution, but the only point of interest is that the liberation of one equivalent of magnesium from a Grignard reagent requires one Faraday (Evans and Lee, 1934). Again, the rapid absorption of oxygen by Grignard reagents in ether solution, and their ready cleavage by halogens are properties that would be expected of intermediate compounds.

The third point is closely connected with the second. If the species in equilibrium with MgX_2 and MgR_2 is in fact RMgX , in which the Mg is in oxidation state +1, no dimerization can be expected, for the 3s electron of the metal ion which is responsible for dimer formation in the simple subhalides of the alkaline earth metals is already paired in the monomer RMgX . In agreement with this, both Schlenk and Schlenk (1926) and Noller and Raney (1940) found that the position of equilibrium in Grignard solutions is independent of total concentration, which indicates that the species in equilibrium with MgX_2 and MgR_2 is monomeric. It might be thought that confirming evidence for this could be

obtained by molecular weight determination, but the work that has been done in this regard indicates that interpretation of boiling-point data is difficult.* There is, however, no good evidence against the view that at normal concentrations the species in equilibrium with MgX_2 and MgR_2 is the monomer RMgX .

The position is, then, that all available evidence is consistent with the Schlenk and Schlenk hypothesis. On the basis of this hypothesis, which is now generally accepted, even by those who formerly preferred an alternative view (e.g. Noller, 1940) reaction mechanisms can in general be explained, notwithstanding difficulties which are inevitable on any view. This hypothesis will therefore be assumed to be correct, and the following description will be taken to characterize the formation of a Grignard reagent:

A Grignard reagent is formed by the reaction of magnesium metal with an alkyl or an aryl halide, in the course of which the magnesium is oxidized by the halogen from oxidation state 0 to +1, the intermediate state being stabilized by pairing of the 3s electron of the Mg^+ ion with the free electron of the R radical, forming an organomagnesium subhalide of formula RMgX . The subhalide is in disproportionation equilibrium with the species R_2Mg and MgX_2 .

There is further evidence for the existence of magnesium ions of oxidation state +1 in ether solution. Evidence for the existence of the equilibrium



in ether-benzene solutions of magnesium iodide in contact with metallic magnesium was put forward by Gomberg and Bachmann (1927) and Gomberg, Bailan and Van Natta (1929). It was shown that ether-benzene solutions of this type reduce aromatic ketones to the corresponding pinacols, often in quantitative yield, a reaction that is not effected by either Mg or MgI_2 alone. This is ascribed to the formation of a halomagnesium ketyl R_2COMgX by combination of the ketone with the intermediate MgK , followed by dimerization to give a halomagnesium pinacolate, $\text{XMgC(R}_2\text{)C(R}_2\text{)MgX}$. The deep colour (usually red) of the reaction mixture is probably due to the colour of the ketyl; this is supported by the facts that the colour is easily destroyed by a trace of oxygen, and that the solutions do not obey Beer's law. The analogy between this reaction and the formation of sodium ketyls has been pointed out by Gomberg and Bachmann.

It has been suggested that the formation of carbinols by interaction of Grignard reagents with ketones has a free radical mechanism, involving the intermediary formation of halomagnesium ketyls of the type discovered by Gomberg and Bachmann (Blicke and Powers, 1929). This cannot be the case, for in reactions of this sort no appreciable quantities of R-R compounds of any sort are formed. In this connection it is interesting to note that under conditions in which the $2\text{Mg}^+ \rightleftharpoons \text{Mg} + \text{Mg}^{2+}$ equilibrium would be expected to shift far to the right, without any net oxidation or reduction taking place, a Grignard reagent splits up, yielding R-R compounds, indicating the liberation of free radicals in the process. Thus it was shown by Colburn (1940) that addition of a catalytic quantity of water to an ether solution of phenylmagnesiumbromide resulted in the formation of large amounts of diphenyl. This appears to be a general reaction.

Finally, it may be observed that although some perplexities have arisen in Grignard chemistry owing to the fact that in many cases the treatment of carbonyl compounds with MgR_2 or with a Grignard reagent RMgX yields substances which give identical hydrolysis products (e.g. the discovery of Noller, 1931, that ether solutions of di-isobutyl magnesium which are practically halogen-

* Terentiev (1926) has published data which do not appear to be in accordance with this, but the methods employed by this author have been criticized by Meisenheimer and Slichenmaier (1928).

free reduce benzophenone to benzohydrol as well as the original Grignard reagents) reactions of this sort are not to be taken as evidence against the existence of RMgX , in which the magnesium is in the intermediate oxidation state, in Grignard solutions. The action of water on both RMgX and R_2Mg results in (i) oxidation of the magnesium (from oxidation state 0 or +1) to oxidation state +2; (ii) reduction of the organic radical R. Difference in the nature of the final products will be expected only when the initial reaction with the carbonyl compound modifies the R groups of either the carbonyl compound or the Grignard reagent. In general this modification will be expected in the action of the Grignard reagent, rather than R_2Mg , on the carbonyl compound, owing to the large I_s effect of the magnesium ion. Thus according to Bartlett and Berry (1934) cyclohexene oxide reacts with Et_2Mg and Me_2Mg without rearrangement to give, on treatment with water, respectively *trans*-2-ethyl and *trans*-2-methyl cyclohexanol. With the corresponding Grignard reagents, cyclohexene oxide yields ethyl- and methyl-cyclopentylcarbinol. Even if this order is sometimes reversed—i.e. if rearrangement occurs in the dialkyl magnesium reaction rather than the Grignard reaction—the difference of mechanism has still to be understood as a difference in type of reaction between a carbonyl compound on the one hand and an organomagnesium compound in which the magnesium is in oxidation state either 0 or +1 on the other.

SUMMARY.

The evidence for the existence of disproportionation equilibria involving +1 ions of the alkaline earth metals is reviewed. It is concluded that these equilibria exist in aqueous and non-aqueous solution, and in the solid and vapour states. Wherever possible, thermodynamic quantities are calculated. The role of these equilibria in reactions involving the alkaline earths is pointed out, and important points of connection between the study of disproportionation equilibria in the organic and the inorganic fields are indicated.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART IV. GEOLOGY OF THE GUNNEDAH-CURLEWIS DISTRICT.

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With Plate XVI.

(Presented by permission of the Under-Secretary for Mines.)

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INTRODUCTION.

The Gunnedah-Curlewis district is by far the most important section of the North-Western Coalfield from an economic point of view. Apart from Werris Creek, it is the only section in which coal mining has developed beyond the prospecting stage and which contains any appreciable reserves. A considerable amount of field-work has been concentrated in this section and most of the area shown on Plate XVI has been surveyed in close detail by means of a telescopic alidade and plane table.

Field-work commenced in 1945, continued throughout almost the entire field season in 1946 and part of 1947, and was completed this year. Several departmental reports have been made by the writer during the course of the present survey, and these contain information concerning coal production, the quality of the coal seams, prospecting, and history of mining operations. In these reports the correlation of the geological sequence with the type area in the Hunter Valley was based on the Werrie Basalts being of Upper Marine age. However, the geological survey of the Willow Tree district (Hanlon, 1947*a*, 1947*b*) showed that the Werrie Basalts form part of the Lower Marine Series, and this has necessitated a reclassification of much of the sequence.

Reports made prior to the present survey were by David (1886), Stonier (1890*a*, 1890*b*, 1893), Pittman (1897), Carne (1908), Harper (1911, 1925) and Kenny (1927, 1928). Professor L. A. Cotton made three private reports to the Gunnedah Colliery Co., which have been kindly made available to the writer.

TOPOGRAPHY AND ACCESS.

Gunnedah and Curlewis are both situated on the North-Western Railway line, being 295 and 285 miles respectively from Sydney. Access by road is good and main roads connecting with Tamworth, Narrabri, Coonabarabran and Quirindi are trafficable in all weathers. Some secondary roads, which cross black soil plains, become impassable after heavy rains.

The Namoi River and its tributary, the Mooki River, flow through mature valleys. Large areas of gently sloping alluvium occur along both rivers at a general level about 900 feet above sea level. Gunnedah, the main town in the district, is 876 feet A.S.L. and Curlewis 897 feet A.S.L. The river flat widens considerably to the north of Curlewis and extends westwards over the Booloo-cooroo Plain.

Most of the high points in the district are capped by dolerite. However, many of these cappings were probably intruded in the form of sills and occupy

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their present positions due to subsequent erosion of the overlying sediments. It is considered that the present high ground formed areas of relative relief in Tertiary time when the dolerites were intruded. This point is elaborated later when considering the Tertiary igneous rocks.

The highest point in the district is King Jack Trigonometrical Station on Black Jack Mountain and is approximately 2,470 feet A.S.L. or 1,600 feet higher than Gunnedah township. A considerable part of Black Jack Mountain is over 2,000 feet A.S.L. and many hills rise to the 1,600 feet level.

Within the hills the creeks occupy narrow steep gullies, but, on reaching the plain level, many of them lose their identity and do not possess any defined channels extending to the Namoi or Mooki Rivers.

GEOLOGY.

The geological formations comprise the following :

Tertiary to Recent alluvium.

Tertiary Igneous Rocks.

Triassic.

Permian

Upper Coal Measures—Black Jack Formation.

Upper Marine Series (?)—Gladstone Formation.

Upper Marine Series—Porcupine Formation.

Lower Coal Measures(?).

Lower Marine Series.

It was originally considered that a group of acid lavas and tuffs which outcrop in and around Gunnedah were of Carboniferous age, but later work has shown that these rocks are interbedded with the Werrie Basalts and should be regarded as being of Lower Marine age. The nearest outcrops of Carboniferous rocks to the Gunnedah district occur in the Carroll area (Lloyd, 1933), east of the more westerly of the Mooki Thrusts. The formations listed above will now be described in order, commencing with the oldest.

Permian.

Lower Marine Series. The Lower Marine Series at Gunnedah comprises a group of lavas and tuffs of acid to intermediate composition, interbedded with amygdaloidal basalts, and discontinuous lenticular beds of sediments which are probably of fresh water origin. No marine fossils were found anywhere in this series in the Gunnedah-Curlewis district. The flows are considered to be the equivalents of the Boggabri Volcanics. (See Part VI of this series of papers.)

The lavas and tuffs are mainly rhyolites or felsites, but trachytes and andesites also occur. Although they form solid outcrops, micro-sections show them to be very much altered. The rhyolites tend to be porphyritic and many of them show well-developed flow structure. In some cases relics of spherulitic structure are present. The phenocrysts are badly altered and in some instances are entirely replaced by chalcedony and opaline silica. Micro-sections of the trachytes and andesites show them to be similarly altered. The flows are lenticular and the proportion of the total thickness of the Lower Marine section which they form varies markedly from place to place.

The amygdaloidal basalts are interbedded with the lavas and tuffs described above. They are all more or less decomposed and micro-sections reveal that they consist chiefly of felspar laths and contain relatively little ferro-magnesian minerals. The amygdules comprise mainly natrolite, calcite and chalcedony. It is considered that they are to be correlated with the Werrie Basalts, and the age of the whole group of lavas, tuffs, amygdaloidal basalts and sediments is therefore fixed as being Lower Marine (Hanlon, 1947*a*, 1947*b*). The maximum

thickness of Werrie Basalts exposed in the Gunnedah district is 450 feet, along and to the west of the railway line south-west of Gunnedah township; The total thickness may be considerably greater, because it appears likely that the black soil plains to the east would be underlain by them, at least in part. The thickness of the Werrie Basalts varies considerably and immediately south and south-west of Gunnedah the section exposed along the railway line appears to have lensed out completely, Greta (?) sediments resting directly on Lower Marine sediments, which in turn overlie the rhyolites that outcrop in the town itself. Adjacent to the Mullaley Road, Upper Marine sediments rest directly on Lower Marine rhyolites.

The sediments comprise sandstones and conglomerates which are generally unfossiliferous. The only fossils found were fragments of *Glossopteris* in an isolated outcrop in portion 364, Parish of Gunnedah, County of Pottinger. The thickness of the sediments and their distribution is very irregular. An explanation would be that the Lower Marine lavas suffered contemporaneous erosion, the Werrie Basalts being removed in preference to the more resistant acid lavas, and irregular beds of sediments were deposited in the drainage channels and depressions so formed. The irregular thickness of the Werrie Basalts would thus be explained as being due partly to their having flowed over lower ground around the thickest acid lava flows and partly to having been eroded themselves and the drainage channels so formed filled with sediments. Alternatively, the Werrie Basalts may have been partly intrusive, an origin suggested for spilites in the Silverwood district and other parts of the world (Bryan, 1925).

Lower Coal Measures (?). There is a restricted outcrop to the south of Gunnedah, of shales containing abundant impressions of *Glossopteris*. There is no evidence of any coal seams being developed. The shales outcrop best in portions 202 and 209, Parish of Gunnedah. In portion 209 they appear to overlie directly the Lower Marine sediments, referred to above, in the region of their maximum development. In portion 202 they are underlain by basalt, which outcrops in the bed of a creek and is very much decomposed. It is probable that the outcrop forms part of the Werrie Basalts.

The shales are lenticular and their development dies out easterly, where the Werrie Basalts are overlain directly by definite Upper Marine sediments and westerly where the Upper Marine is resting on Lower Marine rhyolites. The shales have been classified as Lower Coal Measures because they contain *Glossopteris* and lie between Lower Marine beds and definite Upper Marine sediments. They could, however, represent the final phase in the development of the fresh water sediments which occur in the Lower Marine Sequence or a local development of fresh water sediments during Upper Marine time, prior to the onset of marine sedimentation throughout the area.

Upper Marine Series. It is proposed to name the definite Upper Marine beds the Porcupine Formation. It consists mainly of sandstones with beds of conglomerate. Bands of limestone occur near the top of the sequence, but shales are present only to a minor extent. The occurrence of an erratic containing *Spirifer disjuncta* Sowerby proves that there was contemporaneous ice action, which also probably contributed to the poor sorting of the sediments in some places. There are two main areas of development, one immediately west and south of Gunnedah, especially in the Porcupine Hill area adjacent to the North-Western Railway line, where they form a prominent escarpment 400-500 feet above rail level, and the other to the east and south-east of Curlewis. They form a belt to the north-east of the Upper Coal Measures and probably underlie the alluvium of portion of the Booloocooroo Plains.

Kenny (1928) classified the beds near Gunnedah with the Upper Coal Measures, although he suggested (unpublished report) that they may form part

of the Upper Marine Series. The fossils discovered during the course of the present survey place the marine origin of the beds beyond doubt. The most comprehensive suite of fossils was obtained from portions 195 and 196, Parish of Curlewis, County of Pottinger, and contained the following :

Crinoid stems.

Fenestrellina spp.

Protoretepora ampla Lonsdale.

Stenopora tasmaniensis Lonsdale.

Astartila danai de Koninck.

Strophalosia gerardi King.

Strophalosia jukesi Etheridge.

Spirifer duodecimcostata McCoy.

Aviculopecten sprengi Johnston.

Deltopecten subquiquelineatus McCoy.

Terrakea brachythæra (Sowerby).

Terrakea fragile (Dana).

Dielasma inversa de Koninck.

Conocardium australe (Morris).

Ptychomphalina morrisiana McCoy.

? *Pleurotomaria morrisiana* McCoy.

? *Platyschisma* sp. nov.

Mr. H. O. Fletcher (private communication) states : " In the above Permian fauna there is an abundance of the genus *Strophalosia* and *Terrakea*. This association is somewhat characteristic of the fossil fauna found in the Muree Stage of the Upper Marine Series and in equivalent beds of the Illawarra district. In all probability the marine beds at Curlewis are of a similar age."

Marine fossils have been found at several localities near Gunnedah. The forms listed below were found on horizons near the top of the Porcupine Formation at the following places :

Near the western boundary of portion 314, Parish of Gunnedah, County of Pottinger.

Spirifer duodecimcostata McCoy.

Spirifer sp. indet.

" *Martiniopsis subradiata* " Sowerby (plicated form).

" *Martiniopsis subradiata* " Sowerby (smooth form).

Spirifer cf. *darwini* Morris.

Astartila danai de Koninck.

Edmondia intermedia de Koninck.

Deltopecten subquiquelineatus McCoy. var. *delicatula* Fletcher.

Deltopecten leniusculus (Dana).

Platyschisma rotundata Morris.

? *Pleurotomaria subcancellata* Morris.

On road west of the boundary between portions 310 and 312, Parish of Gunnedah.

Terrakea fragile Dana.

Spirifer duodecimcostata McCoy.

On road between portions 313 and 315, Parish of Gunnedah, about 10 chains from their western boundaries.

" *Martiniopsis subradiata* " Sowerby.

On road south of the boundary between portions 321 and 322, Parish of Gunnedah.

Spirifer duodecimcostata McCoy (abundant).

" *Martiniopsis subradiata* " Sowerby.

Ptychomphalina morrisiana (McCoy).

Indet. pelecypod.

A band of impure limestone, underlying the horizon from which these forms were obtained yielded a doubtful specimen of *Glossopteris*.

The following forms were collected from a lower horizon in the Upper Marine sequence to the west of the scarp in portion 116, Parish of Gunnedah.

Martiniopsis subradiata var. *braxtonensis* Etheridge.

Dellopecten fittoni (Morris).

Spirifer vespertilio Sowerby.

Merismopteria ? macroptera (Morris).

Nearby, to the east of the scarp overlooking the railway line, and on a similar or perhaps lower horizon, abundant specimens of *Edmondia nobilissima* de Koninck and *Edmondia intermedia* de Koninck, together with one incomplete specimen of *Cardiomorpha gryphoides* de Koninck, were collected. The occurrence of these three forms in association to the exclusion of other forms, might suggest that the beds are of Lower Marine age, but mapping has placed them definitely with the beds which have been mapped as Upper Marine. Specimens of *Edmondia* have been collected along the Upper Marine forms from portion 314, Parish of Gunnedah, and also in a suite of fossils containing typical Upper Marine forms from portion 80, Parish of Eulah, County of Nandewar, so that the association is apparently not uncommon in the Upper Marine of the North-western Coalfield.

Overlying the Porcupine Formation there is a group of beds which it is proposed to name the Gladstone Formation. It is at least 300 feet thick and consists almost entirely of shales with odd thin bands of sandstone and carbonaceous or coaly matter. Towards the top the beds are more sandy and there are several thin bands of limestone.

The Upper Coal Measures were originally thought to consist of two groups, an upper one, which is described below under the Upper Coal Measures, and a lower one, the Gladstone Formation. However, no fossils, neither marine nor fresh water, were found in the beds comprising the Gladstone Formation.

The discovery of Upper Marine fossils near Breeza (see Part V of this series of papers) in thin beds of limestone which are developed at the top of a group of shales, makes it probable that the Gladstone Formation is of Upper Marine age. If it is not, it means that 300 feet or more of shales, representing the Gladstone Formation, have thinned out completely between Gunnedah and Breeza, and in the Breeza area up to 500 feet of shales are developed at the top of the Upper Marine sequence and are not represented in the Gunnedah district.

Shales corresponding to the Gladstone Formation probably underlie the alluvium along the railway line between Curlewis and Nea Siding and also over a considerable portion of the Booloocooroo Plains.

Upper Coal Measures. The description is confined to the upper of the two groups referred to above, which is definitely of fresh water origin. It is proposed to name this group the Black Jack Formation, because of its typical development in the vicinity of Black Jack Mountain. It has a maximum thickness of about 550 feet and consists of sandstones, shales, conglomerates, cherts and thin bands of limestone. It contains two coal seams which are of commercial grade and thin or poor quality seams are found on several other horizons. The detailed alidade survey has been concentrated mainly on this formation. *Glossopteris* and *Vertebraria* are abundant and Stonier (1890a) commented that at Curlewis the latter is generally vertical with respect to the stratification.

The Black Jack Formation can be conveniently divided into three zones by the two coal seams. The upper seam is being worked by the Gunnedah and Preston Extended Tunnel Collieries and has been prospected at Pryor's Well and other points. It is proposed to refer to this seam as Hoskisson's Seam and the lower seam as Melville's Seam. The latter has been prospected at Gladstone's adit, in a shaft adjacent to the Gunnedah Colliery Main Adit, in an inclined shaft

near the old Preston Colliery Adit, and in Melville's Well. Hoskisson's Seam is up to 16 feet thick at some points, but the worked section is about 7 feet 6 inches thick. The coal is of high quality, the ash content being about 7% and the calorific value 13,600 B.Th.U.'s per pound. Melville's Seam is lower in grade and has a maximum thickness of about 8 feet, including bands. The ash content is about 15% and the calorific value 11,400 B.Th.U.'s per pound. However, better quality coal could be obtained from this seam by excluding certain bands.

The lowest zone of the Black Jack Formation, below Melville's Seam, is about 70 feet thick adjacent to Gunnedah Colliery. It consists of shales overlying a band of sandstone approximately 40 feet thick.

The zone between Hoskisson's and Melville's Seams consists of shales with several well marked bands of sandstone. None of the bands is in any way distinctive from the others, but outcrops of individual bands can be traced over considerable distances and form very useful beds in mapping. The zone is 190 feet thick in the Gunnedah district but at Curlewis it has thinned down to 150 feet. Outcrops are developed best in the area between the Gap and Little Sugarloaf. At Curlewis the inclined shaft to test Melville's Seam intersected 2 feet 6 inches and 1 foot of coal, 60 and 80 feet respectively above Melville's Seam. The shaft which was sunk to Melville's Seam at Gunnedah Colliery intersected 6 inches of coal, 36 feet above the seam. Near Little Sugarloaf there is also evidence of carbonaceous material at a level 35 feet above the seam. Between Little Sugarloaf and the Gap there are outcrops of weathered coaly material at several points about 70 feet above Melville's Seam.

The thickness of the beds above Hoskisson's Seam varies between 240 feet in the vicinity of Gunnedah Colliery to 300 feet in the Curlewis area. The zone contains several horizons that are worthy of particular mention.

The lowest horizon consists of a band of pale buff to terra-cotta coloured cherty claystones and shaley sandstones, which are up to 40 feet in thickness. Their development is spasmodic and they appear to owe their origin to the alteration, by igneous activity, of shales which overlie Hoskisson's Seam. In some places where the shales have been intruded by basalt the resultant rock consists of a breccia composed of cherty fragments in a basaltic cement. The main development of these beds is in the Gunnedah area south of McCosker's Adit and north and north-west of the mine workings. Their absence overlying the seam in the immediate vicinity of the main adit of the Gunnedah Colliery is no doubt due to the fact that the coal measures at this point have not been intruded by sills of dolerite. The development of these cherty beds is mainly confined to the one horizon, but local developments of similar beds do occur at odd points below Hoskisson's Seam.

Overlying the horizon of the cherty claystones is a band composed mainly of sandstone which is characterized by the presence of white quartz pebbles in certain beds. The pebbles are confined almost entirely to this band and the occurrence of abundant white quartz pebbles on other horizons within the coal measures is rare. However, exact correlation within the band is not always possible because the maximum development of the pebbles seems to be concentrated at different horizons in different places, and the thickness of the band appears to vary. Within the Gunnedah Colliery holding the band is about 100 feet thick and the base lies 50 to 60 feet above Hoskisson's Seam. On the other hand near the old Preston Mine at Curlewis, the band is only of the order of 25 feet thick and the base is only about 25 feet above Hoskisson's Seam. The occurrence of sandstone containing white quartz pebbles within the coal measures is, however, an excellent indication that the horizon in question is stratigraphically above the horizon of Hoskisson's Seam.

About 30 feet above the pebbly sandstone there is a band of chert which forms a very useful key horizon. Near McCosker's Adit within the Gunnedah

Colliery holding the band is 170 feet above Hoskisson's Seam and about 70 feet below the base of the Trias. However, care has to be taken when using this bed for correlative purposes not to confuse it with a higher band of cherts and cherty shales which occurs close to the base of the Trias. This upper band is particularly well developed west of Black Jack Mountain, in the Wondobah State Forest area, and to the south of Curlewis. It contains excellently preserved plant remains. The following forms have been recognized in specimens from Wondobah State Forest.

Glossopteris indica Schimper.

Glossopteris browniana Brong.

Glossopteris ampla Dana.

Gangamopteris cyclopteroides Feistmantel.

About half-way between the two chert bands, there is a bed of conglomerate which is developed in both the Gunnedah and Curlewis areas. Above the Gunnedah Colliery Adit the bed is 180 feet above Hoskisson's Seam and 60 feet below the base of the Trias. (At this particular point the middle band of chert is only 145 feet above the seam.) Near Preston Colliery Adit it is 170 feet above the seam and 130 feet below the Trias.

There is a very interesting local development of a thin band of impure limestone in the area west of Black Jack Mountain. It occurs close to the top of the coal measures and as far as is known it is unfossiliferous. It is concretionary in part and in some places pieces closely resemble *Stenopora* although it is apparently an inorganic structure. How far it extends westwards under the Triassic rocks it is impossible to say. Another thin band of limestone outcrops at a lower stratigraphical level on the eastern slope of Black Jack Mountain north of the Gap, but seems to have a very restricted areal development.

Silicified wood is very well developed, particularly on two main horizons. One of these is immediately overlying the sandstone with white quartz pebbles. Excellent examples from this horizon are to be found in portion 56, Parish of Black Jack, near the north-western corner of portion 39. The other horizon is close to the top of the measures to the west of Black Jack Mountain in the Parish of Gill.

Coaly matter has been reported at several horizons above Hoskisson's Seam. Carne (1908) reports the occurrence near Curlewis of a seam 5 feet thick, 100 feet above Hoskisson's Seam and a second seam composed of coal and bands 12 to 15 feet thick, a further 90 feet higher. A water bore sunk between Preston and Preston Extended Tunnel Collieries recorded coal at 55 and 85 feet above Hoskisson's Seam, but another bore near by which penetrated the same strata showed no record of coal in these positions. Professor L. A. Cotton (private report) records a thin seam of coal, 9 inches thick, 75 feet above Hoskisson's Seam. West of Black Jack Mountain in portion 13, Parish of Gill, a band of carbonaceous material occurs close to the base of the Trias.

There is a local development of andesitic breccia immediately underlying the Triassic conglomerate on Sugarloaf Mountain in portion 160, Parish of Gunnedah. The rock is obviously of a fragmentary nature and both the fragments and matrix are of similar composition. The upper contact appears to be regular but the lower contact is irregular and the underlying coal measures appear to be faulted. The bed thins considerably towards the north. The junction between the breccia and the overlying Triassic beds is very well exposed in some places. The breccia is cemented to the Triassic conglomerate and the contact resembles a chilled margin. The marginal portion of the breccia is somewhat altered and iron-stained but microscopical examination shows that it is composed of brecciated material similar to the main mass. The alteration, iron-staining and cementation to the Triassic conglomerate may be the result of leaching by ground waters moving along adjacent to the contact with redeposition of iron oxides to give a

banded appearance. The bed is probably a flow breccia which was erupted about the close of the Permian era. The only other outcrop of similar material in the area is a small isolated one on the top of a hill composed of coal measures in M.L. 5, Parish of Gunnedah. If it were not for the fragmentary nature of the material on Sugarloaf Mountain it would be natural to group it with the Tertiary intrusives and classify it as a sill. However, in order to do this, it would be necessary to explain the brecciation as being due to movement during solidification.

Several examples of intrusive tuffs have been referred to by Browne (1929) and Mr. E. J. Kenny (unpublished report) records the occurrence of intrusive rocks which microscopical examination show to have the composition and texture of arkoses. However, it would probably be even more difficult to explain the mechanics of the intrusion of a coarse breccia, especially if a considerable time break be postulated between the deposition of the intruded sediments and the period of the intrusion.

Triassic.

The Triassic beds mapped consist of conglomerates and sandstone. Shales, several hundred feet thick, have been recorded by Mr. E. J. Kenny (unpublished report) in bores which have been sunk for water in the vicinity of Haystack Mountain, to the west of the area mapped.

The conglomerates and sandstones have been named the Digby Beds by Kenny (1928). The basal beds consist of conglomerates and are characterized by the presence of abundant pebbles of red jasper. The conglomerates differ sufficiently from other conglomerates which outcrop in the district to make them readily recognizable and form a very valuable horizon for mapping purposes, enabling the upper limits of the Permian System to be delineated accurately. They are noteworthy for the presence in them of boulder beds, many of the boulders being more than a foot in diameter. The boulder beds are very well developed to the west of Black Jack Mountain in the Parish of Gill. The coarse conglomerates grade upwards through fine conglomerates and sandstones with pebbly bands, into the overlying sandstones. They vary in thickness between 20 and 100 feet, and average about 30 to 40 feet.

The sandstones are generally thinly bedded and outcrop over wide areas, being considerably thicker than the conglomerates. Their upper limits were not mapped during the present survey.

Thin beds of fine-grained rhyolite breccia and decomposed volcanic breccia have been found in a few localities, the main ones being in the Parish of Digby and in Wondobah State Forest.

No fossils were found in the Digby Beds anywhere in the area, and following Kenny they have been classified as Triassic. They are similar to beds in neighbouring areas to the south-east which have been previously classified as Triassic.

Tertiary.

The Tertiary rocks are entirely of igneous origin and comprise olivine and analcite dolerites and olivine and nepheline basalts. They occur as sills, dykes and flows, and form cappings to most of the high hills in the district. The cappings mostly consist of fairly coarse-grained dolerites and were probably intruded as sills under a thin cover of sediments which have been subsequently eroded. Sills have been found intruding all formations in the district except the Upper Marine. In some places the sills may have passed laterally into flows.

The disposition of the sills appears to be related to the topography. Along the main portion of Black Jack Mountain they are common in the Triassic rocks but relatively little developed through the coal measures. The dolerite reaches its maximum development in the vicinity of King Jack Trigonometrical Station

where altogether there must be a total thickness of the order of 1,000 feet. East and west of Black Jack Mountain the coal measures have been extensively intruded by sills of dolerite. These sills have already had considerable influence on the development of the coal resources of the district and will continue to do so in the future. Beyond the northern limits of the outcrops of the Triassic rocks along Black Jack Mountain, it is found again that the coal measures have been affected by igneous activity. Because the intrusion of sills depends on the ability of the igneous material to lift the overlying strata and hence on their thickness, the disposition of the dolerite sills in relation to the present topography would indicate that relatively high ground in Tertiary time occupied approximately the same positions as the present areas of relief.

In many places the sills have broken through from one level to another, thus giving a complex shape to the intrusive mass. Dolerite and basalt talus tends to be scattered over the hill slopes, often completely obscuring outcrops of sediments. The combination of the above effects renders accurate mapping of boundaries very difficult and in some places impossible. No attempt has been made to map many isolated outcrops of Triassic sandstone which occur along the higher levels of Black Jack Mountain.

Dykes occur as a network in some areas and probably formed the main feeders by which the sills were intruded. Professor L. A. Cotton (private report) gives the dominant direction of the dykes as south-westerly, with a second direction of minor importance about N. 20 W. and a third direction of still lesser importance trending slightly north of west. The dykes are probably more numerous in areas where sills or flows of dolerite are present.

West of the area shown on the map (Plate XVI) there is a widespread development of olivine and analcite dolerites which have been mapped as Garrawilla (Jurassic) flows. When examined microscopically they are found to be identical with typical Tertiary dolerites. It is considered that it would be preferable to classify most of these rocks as Tertiary sills as originally proposed by Kenny (1927) rather than as Jurassic flows.

Tertiary to Recent.

These deposits are confined to the alluvium along the Namoi and Mooki Rivers and their tributaries. The main development is in the Booloocooroo Plain and the area to the east, across to the Mooki River.

The alluvium consists of "black soil," red clay, sandy clay, sands and gravels. East of the belt in which the Upper Marine beds occur the alluvium may be largely underlain by Werrie Basalts.

STRUCTURAL GEOLOGY.

The structural geology is relatively simple when compared with that of the sections of the North-western Coalfield described previously in this series of papers. The Gunnedah-Curlewis district is wholly situated to the west of the Hunter-Mooki zone of thrust-faulting. The structure consists of minor folding and faulting which has been superimposed on a general dip to the south-west.

Structure contours on the base of the Upper Marine Series show that a small basin exists in the position where the *Glossopteris*-bearing shales are developed near Gunnedah. This relationship could be explained in either one of two ways. First folding may have commenced at the time the shales were being deposited and they could represent a local development in a small basin formed in this manner. If this were so it might have been expected that the folding would have tended to persist to some extent into Upper Marine time and be reflected in a local thickening of the overlying strata. However, as the overlying Upper Marine beds have been removed to a large extent in this section

by erosion, it was not possible to obtain evidence either for or against this contention. Secondly, it may be that the position of a small basin developed during later folding may have been influenced so as to be located where there was a local development of underlying sediments.

The detailed alidade survey has disclosed minor folding in which both the Triassic and Upper Coal Measures have participated, and which a reconnaissance survey would have failed to reveal. If suitable key beds could be found in the Triassic beds further west, similar detailed surveying may disclose minor folding of a like nature. The apparent simplicity of structure in many of the areas occupied by Triassic rocks is probably due to the lack of outcrops of suitable key beds and sufficient detailed survey work.

The most interesting structure in the Triassic rocks is an undulating anticlinal zone which has been superimposed on the general dip and accounts for the zone of isolated outcrops of the Upper Coal Measures to the west of Black Jack Mountain in the Parish of Wondobah. This zone continues northwards into the Parish of Gill and south-eastwards into the Parish of Digby.

Many of the folds and small faults which exist in the district are certainly younger than Triassic Digby beds. Some, at least, of the faults appear to be associated with the intrusion of the Tertiary dolerites.

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SUMMARY.

The Permian sequence comprises Lower Marine lavas and subordinate fresh water sediments, Greta Coal Measures (?), Upper Marine Series and Upper Coal Measures. It is overlain conformably by Triassic conglomerates and sandstones. Sills, dykes and flows of Tertiary dolerite form extensive outcrops and there are also extensive alluvial areas. The general dip is south-westerly and on it minor folding, which has affected both Permian and Triassic beds, has been superimposed.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART V. GEOLOGY OF THE BREEZA DISTRICT.

By F. N. HANLON, B.Sc., Dip.Ed.

Geological Survey of New South Wales.

With Plate XVII.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The area covered by this paper extends from the Gunnedah-Curlewis district (Hanlon, 1948), which it adjoins on the north, to about four miles south of Breeza. The survey was in the nature of a detailed reconnaissance. Spot heights on the base of the Triassic between Curlewis and Nea Siding were established by resections and an alidade traverse was made from the railway line in the vicinity of Breeza, across to the Triassic conglomerate near Watermark Trigonometrical Station, and thence to the north-western corner of portion 144, Parish of Breeza, County of Pottinger, where Upper Marine limestones outcrop.

TOPOGRAPHY AND ACCESS.

Breeza is situated on the North-western Railway line, being 269 miles from Sydney and 953 feet above sea level. Access by road is good, although many of the roads are not gravelled and are impassable after any appreciable rain. The area is wholly situated within the County of Pottinger.

The Mooki River, which flows immediately to the east of Breeza, is the main stream in the district. It is a tributary of the Namoi River, which it joins near Gunnedah. Other streams are only insignificant.

The district is bounded on the east and south by alluvium, and large sections of the north and west are also alluviated. Relief is moderate, the highest points being Cockroft and Watermark Trigonometrical Stations, 1,885 and 1,678 feet above sea level respectively.

GEOLOGY.

The geological formations of the district comprise the following, which will be described in order, commencing with the oldest:

Tertiary to Recent alluvium.

Tertiary Igneous Rocks.

Triassic.

Permian.

Upper Coal Measures.

Upper Marine Series.

Permian.

Only the Upper Coal Measures and Upper Marine Series are represented in the Breeza district. The Lower Marine lavas which are so well developed further north around Gunnedah and Boggabri do not outcrop, but the Werrie

Basalts (Lower Marine) may underlie a large portion of the Breeza Plains to the east.

Upper Marine Series. Only the upper beds are exposed and it is only thin limestone bands which form recognizable outcrops. From bore records it appears that the underlying beds are composed mainly of shales. These shales form very poor aquifers and supplies of water obtained are almost invariably salt.

In the Parish of Breeza, within Portion 144 and the south-western corner of Portion 155, thin bands of fossiliferous limestone outcrop. The following forms were found :

Aviculopecten multicostatus Fletcher.

Platyschisma ocula Sowerby.

Astartila danai De Kon.

Mytilus cf. *bygsbyi* De Kon.

Deltopecten ? *fittoni* (Morris).

? *Notomya cuneata* Sowerby.

? *Stutchburia costata* (Morris).

? *Spirifer* sp.

Pelecypod. (Resembles an undescribed form found low in the Branxton Stage of the Upper Marine Series.)

It is proposed to name the shales and interbedded limestones the Watermark Formation because its typical development is in the neighbourhood of the railway platform and trigonometrical station of that name. It is in no way comparable with the fossiliferous Upper Marine sandstones and conglomerates (the Porcupine Formation) in the Gunnedah-Curlewis district (Hanlon, 1948). It is considered unlikely that such a complete facies change would take place between Nea Siding, adjacent to which the Porcupine Formation outcrops, and Watermark, a distance of only three miles. This probably means that the Watermark Formation represents a subsequent development to the Porcupine Formation and suggests that it should be correlated with the Gladstone Formation of the Gunnedah district. As stated previously (Hanlon, 1948), the Gladstone Formation is unfossiliferous and was formerly considered to be part of the Upper Coal Measures sequence. It was the suggested correlation with the Watermark Formation which made it likely that the Gladstone Formation might be of Upper Marine Age. Otherwise it is necessary to postulate that in Upper Marine time the 500 feet of shales making up the Watermark Formation either lensed out completely or passed laterally into a thinner group of sandstones and conglomerates (Porcupine Formation), and that subsequently in Upper Coal Measures time, 300 feet or more of shales in the Gunnedah district (Gladstone Formation) lensed out completely in the opposite direction.

Upper Coal Measures. It is considered that the Upper Coal Measures sequence in the Breeza district represents the south-easterly continuation of the Black Jack Formation which was mapped in the Gunnedah-Curlewis district (Hanlon, 1948). In the northern portion of the area mapped the sequence is the same as that of the Black Jack Formation in the type area and consists of sandstones, shales, conglomerates, cherts and coal seams. Besides the species of *Glossopteris* which have been collected in other parts of the North-Western Coalfield, specimens of *Glossopteris conspicua* Feist. were found in cherty shales close to the base of the overlying Triassic conglomerates in Portion 205, Parish of Curlewis. Good specimens of the basal end of the stem of *Phyllothea australis* Brong. were also collected from this horizon.

Further south in the vicinity of Watermark Trigonometrical Station the facies have altered somewhat and part of the upper portion of the sequence is missing. The topmost bed in the coal measures near Watermark T.S. is about ten feet thick and consists of shales with cherty bands. It overlies eighty feet

of sandstones with bands of white quartz pebbles which in turn overlies terra-cotta coloured cherty claystones. It is considered that the last two zones correspond to similar ones in the Gunnedah district (Hanlon, 1948). Whether the overlying cherty shales correspond to the middle or upper band of cherts from the Gunnedah-Curlewis area it is not possible to say. However, whichever band it represents there are strata of the order of 150 feet which are present in the Gunnedah-Curlewis district and are missing from the vicinity of Watermark. The beds appear to be conformable and conditions favour non-deposition of the missing beds rather than their deposition and subsequent erosion.

Coal has been prospected in portions 123 and 89 in the Parish of Breeza and has also been struck in several wells and bores sunk for water. The logs of some of the bores suggest that Hoskisson's Seam is tending to split towards Breeza or that other seams are developed locally on adjacent horizons to it. It is considered that the seam prospected at Breeza is on or about the horizon of Melville's Seam. Associated with it there is a marked development of beds of conglomerate, the pebbles being composed mainly of acid lavas. It is a distinct change of facies compared with the Gunnedah district. Harper (1913) reported on the quality of the coal in portion 123.

Triassic.

The Triassic beds mapped consist of conglomerates and sandstones similar to those described in the Gunnedah-Curlewis district. In the northern section of the area in the Parish of Curlewis, the beds form a characteristic line of cliffs. However, to the south-west of Nea Siding and west of Breeza the conglomerates form poor outcrops, the positions the beds occupy being indicated by the occurrence of very abundant jasper and quartzose pebbles. Actual outcrops of beds of conglomerate are relatively few.

Tertiary Igneous Rocks.

The Tertiary rocks comprise dolerites and basalts and their modes of occurrence are similar to those in the Gunnedah-Curlewis district.

The most noteworthy feature is the occurrence of a sill in the Breeza-Watermark area which is developed at, or slightly below, the horizon which Hoskisson's Seam would occupy if developed. Its position in relationship to beds of buff and terra-cotta coloured cherty shales which underlie sandstones with white quartz pebbles is similar at all points in which the beds have been examined. To the north of Watermark Trigonometrical Station a breccia composed of fragments of chert in a basaltic cement is common.

According to local reports one well sunk in portion 8, Parish of Nea, has the western side formed by a vertical wall of rock (dolerite?), while the eastern side consists of coal measures with a low dip, including coal on three horizons (splits of Hoskisson's Seam?). This suggests that the dolerite is in the form of a dyke, but further west the same mass obviously underlies a band of sandstone with white quartz pebbles, and the intrusion must be concordant in some places and transgressive at others.

Tertiary to Recent.

Alluvium occupies a large proportion of the area mapped. It completely surrounds the area on the east and south and forms large sections to the north and west. It is of the "black soil" variety and on the north and east is probably underlain by Upper Marine shales and Werrie basalts (Lower Marine). Eastwards it extends across the Breeza Plains until it reaches the Carboniferous hills to the east of the Mooki Thrusts (Carey, 1934).

STRUCTURAL GEOLOGY.

As in the Gunnedah-Curlewis district, the structures are relatively simple when compared with the zone of pronounced folding and thrust faulting further to the east.

The main dip is generally in a south-westerly direction except in the Watermark area. Here the structure consists of a dome or a very pronounced nose. It is closed to the west, south and north-east, but to the north it is obscured by alluvium and may or may not be completely closed. It is proposed to name the structure the Watermark Dome. Upper Marine beds outcrop in the core of the dome. North-easterly, southerly and westerly dips occur in the overlying Upper Coal Measures. The folding has affected the Triassic as well as the Permian. However, as described above, much of the topmost portion of the Upper Coal Measures sequence is missing in this area, which indicates that some of the folding was pre-Triassic.

ACKNOWLEDGEMENTS.

I was assisted on this survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. A. B. Walkom, Director of the Australian Museum, for the determinations of the fossil plants, and to Mr. H. O. Fletcher, Palæontologist to the Australian Museum, for the determinations of the marine fossils. I wish especially to thank Mr. J. M. Clift, of Gilgulgul, Queensland, for making available to the writer a collection of marine fossils made by him in the Breeza district. I also wish to express my thanks to Mr. J. E. Lancaster, Under-Secretary for Mines, and Mr. C. St. J. Mulholland, Government Geologist, for permission to publish this paper.

SUMMARY.

Only the upper part of the Permian sequence, comprising the Upper Marine Series and Upper Coal Measures, outcrops in the area. It is overlain by Triassic conglomerates and sandstones. The beds have been intruded by Tertiary dolerites and there are also extensive areas of alluvium. There is a general dip to the south-west except in the Watermark area, where there is a dome which was formed partly in pre-Triassic and partly in post-Triassic time.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART VI. GEOLOGY OF SOUTH-WESTERN PART OF COUNTY NANDEWAR.

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With Plate XVIII.

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INTRODUCTION.

The area geologically surveyed comprises about 350 square miles of territory in the south-western part of the County of Nandewar. It adjoins the main section of the North-western Coalfield along the Namoi River in the neighbourhood of Gunnedah (Hanlon, 1948*a*). Although practically unprospected and hitherto not included within the State's likely coal-bearing areas, the survey has shown that this area represents a potential addition to our coal reserves. It continues the survey of a belt of country in which the eastern margin of the Permian sediments in the North-western Coalfield is situated. This belt extends from the Murrurundi-Willow Tree district (Hanlon, 1947*b*, 1947*c*, 1947*d*), through the Werrie Basin (Carey, 1934, 1935, 1937), to the Gunnedah-Manilla district (Lloyd, 1933). The area mapped adjoins and to some extent overlaps the Gunnedah-Manilla district. The boundaries of the Carboniferous and Devonian rocks south of Round Hill, shown on Plate XVIII, have been taken from the map of the above area.

TOPOGRAPHY AND ACCESS.

The North-western Railway passes to the west of the area through Gunnedah and Boggabri on the Namoi River, 295 and 320 miles from Sydney respectively.

Access by road is good during dry weather, but as many of the roads cross areas of black soil, they become impassable after appreciable rain. Roads connect with Gunnedah and Boggabri on the west and across the range with Tamworth, Manilla and Barraba on the east.

The area is one of medium relief and lies between the valley of the Namoi River on the south and west, and a line of hills to the east, which joins the Nandewar Range further north. The northern boundary is formed by Maules Creek, a tributary of the Namoi River. Much of the area consists of wide areas of alluvium which slope gently towards the Namoi River. Tributaries of the Namoi River, other than Maules Creek, are insignificant.

Gunnedah and Boggabri, which are situated adjacent to the Namoi River, are 876 and 823 feet above sea level respectively. The highest points in the area are situated within Vickery and Leard State Forests and at Mount Goonbri, being 500 to 800 feet above the plain level. The line of hills to the east are somewhat higher and appear to rise northwards towards the Nandewar Mountains.

GEOLOGY.

The geological formations comprise the following :

Tertiary to Recent alluvium.

Tertiary Igneous Rocks.

Permian

Nandewar Group.

Boggabri Volcanics.

Carboniferous

Upper Kuttung Series.

The rocks will now be described in detail commencing with the oldest.

Carboniferous.

The Carboniferous rocks have not been mapped in detail because the survey was concerned primarily with the Permian beds. The Carboniferous-alluvium boundary south of the latitude of Boggabri has been taken from the map of the Gunnedah-Manilla district (Lloyd, 1933).

The rocks outcrop along the eastern boundary of the area surveyed and belong to the Upper Kuttung Series. They consist of acid lavas, tuffs and conglomerates, the lavas comprising rhyolites, porphyritic rhyolites (Lloyd, 1933), felsites, andesites and pitchstones.

A considerable area to the north of Boggabri has been classed as Carboniferous on old maps in the Department of Mines, but these rocks have now been grouped with the Boggabri volcanics described below.

Permian.

The Permian rocks comprise a group of sedimentary beds and a group of lava flows. It is proposed to name the lava flows the Boggabri Volcanics, because their maximum development is adjacent to and north of that town. The sediments have been called the Nandewar Group since they are typically developed within the County of Nandewar.

Boggabri Volcanics. They comprise flows which are considered to be of Lower Marine age because of their similarity to flows, west of the Namoi River at Gunnedah, which appear to form part of the Lower Marine sequence. They have been intruded by later, probably early Tertiary, alkaline rocks, which may be related to the Nandewar Mountain intrusives. The later intrusives have been included with the Boggabri Volcanics for mapping purposes because in the time available no satisfactory separation of the two groups of igneous rocks could be made. Such a separation would entail a considerable amount of careful collecting and the study of many rock sections. The Tertiary alkaline rocks collected are described below under the Tertiary volcanics.

The outcrops of the Boggabri Volcanics consist almost entirely of acid lavas and tuffs, the lavas comprising rhyolites, trachytes, andesites and basalts. This phase of the Lower Marine volcanic activity is much more extensively developed near Boggabri than the corresponding phase at Gunnedah. On the other hand the Werrie Basalts, which are interbedded with the lavas and tuffs and predominate to the south and west of Gunnedah, do not form conspicuous outcrops in the Boggabri area. Saint Smith (1911) records decomposed amygdaloidal basalt on the western side of the Namoi River in M.L. 3, Parish of Boggabri, County of Pottinger.

Nandewar Group. It is proposed to subdivide the Nandewar Group into the Wean formation and the overlying Vickery Conglomerate. Both formations are typically developed within the Parish of Vickery, the Vickery Conglomerate especially so within the State Forest of that name.

The Wean formation is of fresh water origin and contains abundant impressions of *Glossopteris browniana* Brong, *Glossopteris ampla* Dana, *Glossopteris tortuosa* Zeiller, and *Glossopteris* sp. *Noeggerathiopsis hislopi* Feistmantel was also found. As far as the formation is exposed it consists of shales, sandstones and conglomerates with coal seams and is at least 350 feet thick. The shales are ferruginous in places and contain bands of concretionary ironstone. A coal seam 7 feet 10 inches thick (including a two-inch band near the middle) was struck at a depth of 86 feet in a well in portion 12, Parish of Vickery. The seam was lying almost horizontally. The ash content was 12.9% and the calorific value 12,487 B.Th.U.'s per lb. on a moisture-free basis. Many bores for water in the Parishes of Brentry, Vickery, Boggabri, Leard, Bollol and Berrioye have struck coal. However, as the bores were all sunk with percussion plants and the logs were provided by the drillers, any information as to the thickness or quality of the seams is unreliable.

The Vickery Conglomerate consists of pebbles of medium size, although in places boulders up to a foot across occur. Most of the pebbles have been derived from acid lavas. Sandy or shaley facies are developed only to a minor extent. The Vickery Conglomerate is at least 530 feet thick, and in the absence of fossil evidence it is impossible to state definitely that it is not of marine origin. Besides its development in Vickery State Forest, it is also well developed in the higher portions of Leard State Forest and on Mount Goonbri underlying the dolerite capping.

Correlation. In any attempt at correlating the beds with the Permian sequence of the type area in the Hunter Valley, the absence of any marine fossils is a serious difficulty. This leaves as bases for correlation only the plant fossils, lithological sequence, the most likely relationship of the group to known Permian strata in adjacent areas and the rank of the coal. At the best these can be only indications but, provided the evidence is not contradictory, may provide a reasonable tentative correlation.

There are three possible coal-bearing fresh water zones in the Permian sequence with which the Nandewar Group could be correlated, that is, of course, provided it is not considered a fresh water equivalent of beds which are elsewhere only known to be marine. These are the Upper and Lower Coal Measures (Clarke, 1870; David, 1907), and the basal fresh water portion of the Lower Marine series (Hanlon, 1947*b*, 1947*c*, 1947*d*). It is considered impossible to differentiate between the Upper and Lower Coal Measures by means of the flora with any certainty. Although *Gangamopteris* is more plentiful than *Glossopteris* at some places in the Lower Coal Measures, this is not always the case. On the other hand *Glossopteris* appears definitely to be subordinate in the fresh water portion of the Lower Marine. *Gangamopteris cyclopteroides* and *Phyllothea australis* have been recorded from these beds in the Murrurundi district (Hanlon, 1947*d*) and Carey (1935) records *Noeggerathiopsis hislopi*, *Gangamopteris cyclopteroides*, *Gangamopteris* sp. *Glossopteris* cf. *browniana* and *Palaeovittaria McCarthyi* from them in the Werrie Basin. It is considered that the abundance of *Glossopteris* in the Nandewar Group would render its correlation with the basal fresh water portion of the Lower Marine unlikely and that it is at least as young as the Lower Coal Measures.

The lithological sequence differs markedly from that of the Upper Coal Measures in the adjacent Gunnedah area. It could be, of course, that the Vickery Conglomerate represents a coarse marginal phase laid down close to the edge of the Upper Coal Measures basin but this is considered doubtful. In the Breeza area (Hanlon, 1948*b*) conglomerates composed largely of pebbles of acid lava are developed above and below the horizon of the coal seam close to the base of the Upper Coal Measures sequence. However, in the area under considera-

tion the Vickery Conglomerate is apparently developed several hundred feet above the horizons of the coal seams. The closest resemblance which the sequence bears to that of coal measures in other parts of the North-western Coalfield is with Werris Creek (Carne, 1913, 1914; Benson, 1920; Carey, 1934, 1935; Hanlon, 1946), where the measures consist of 350–400 feet of shales, sandstones, conglomerates and coal seams, overlain by 50–100 feet of conglomerates. Here, too, the conglomerate pebbles consist largely of acid lavas, although quartzite is also common. Carey (1935) recorded an abundant *Glossopteris* flora from these beds, plants collected including *Glossopteris browniana*, *Glossopteris indica*, *Glossopteris ampla*, *Noeggerathiopsis hislopi*, *Phyllothea australis* and *Phyllothea* cf. *etheridgei*, and correlated the beds with the Upper Coal Measures. However, as these beds overlie conformably the Werrie Basalts, which are now known to be of Lower Marine age (Hanlon, 1947*b*, 1947*c*, 1947*d*) it is considered that they are more likely to belong to the Lower Coal Measures, as originally suggested by Carne (1913).

At Ashford, too, the Permian sequence comprises coal-bearing beds overlain by conglomerates (Pittman, 1896; Hanlon, 1947*a*). The Ashford Measures are also thought to be of Greta age.

Harper (1909) reported Upper Marine fossils from 14 miles east of Narrabri. It is expected that future work in this area north of Maules Creek may show that the Upper Marine beds overlie the northerly continuation of the Nandewar Group. If this be so it would mean the latter should be correlated with the Lower Coal Measures, which agrees with the suggested correlation of the Nandewar Group with the measures at Werris Creek.

Dr. J. A. Dulhunty has kindly examined microspores from a sample of coal from the Parish of Vickery. He stated (private communication) that: "I was unable to find any of the types which usually characterize the Greta . . . the spore assemblage in the coal in question certainly appeared more like Upper Coal than that of Maule's Creek and Werris Creek materials which could be Greta from their spore contents." It is interesting that although the spore content of the coal in the Wean Formation favours classifying it as belonging to the Upper Coal Measures the spore content of the coals at Maule's Creek and Werris Creek, of whose age there is some doubt, are consistent with a Greta age. It is with these two groups of coal measures that the field-work suggests the Wean formation should be correlated.

The rank of the Permian coals has often been regarded as useful in assisting correlation of coals from different districts. Jones (1939) quotes the following carbon ratios for the Northern Coalfield.

Greta	55.56
Tomage	60.49
Newcastle	61.13

However, the carbon ratios are of no value in differentiating between coals occurring in the Lower and Upper Coal Measures in the North-western Coalfield. Dealing first with the Upper Coal Measures, the carbon ratios of the Upper or Hoskisson's Seam at Gunnedah Colliery is 59.8 and at Preston Extended Tunnel Colliery 59.3. However, individual plies vary between the limits 67.4 and 53.7. The Lower or Melville's Seam at Gunnedah Colliery has a carbon ratio of 59.8 and individual plies vary between 61.2 and 56.7. The seam prospected at Breeza has a carbon ratio of 58.7 (Harper, 1913). Compared with the figures quoted above by Jones, it will be seen that the average carbon ratios lie between those of the Newcastle and Greta Coal Measures, while the upper and lower limits are higher than the figures for the Newcastle Measures and lower than those for the Greta Measures respectively. Considering the figures for the Lower Coal Measures a large variation is again found. The carbon ratios of the

coal seam at Willow Tree are given below. The analyses on which the first five figures are based are quoted by Raggatt (1938). The last two figures are based on analyses supplied by the lessees.

Grab sample from dump by L. J. Jones	63.5
Picked sample from dump	56.3
Upper four feet of seam	56.3
Lower five feet of seam	60.9
Two pieces of bright coal dug out under water in bottom of shaft	52.7
Full section of seam—16 feet	63.8
Do.	51.8

The carbon ratios of the coal from the Werris Creek Colliery is 67.2 and varies between the limits of 59.9 and 68.8.

The carbon ratio of the coal from the well in portion 12, Parish of Vickery, is 63.8. Although this figure is much higher than those for the Greta Measures and is more closely related to those for the Newcastle Coal Measures in the Northern Coalfield, it is similar to or less than those for known Greta coals in the North-western Coalfield.

To sum up, it may be stated that the lithological sequence and possible relationship of the beds to the Upper Marine further north favour correlating the Nandewar Group with the Lower or Greta Coal Measures. On the other hand the spore contents rather favour correlation with the Upper Coal Measures. The fossil flora and carbon ratio of the coal do not favour correlating the beds with either group of coal measures rather than the other, but are not inconsistent with what might be expected in beds of Greta age. It has therefore been decided to assign the Nandewar Group tentatively to the Lower or Greta Coal Measures. The beds were probably laid down in a narrow trough whose main axis trended approximately north-north-west. The Lower Marine lavas to the west in the vicinity of Boggabri and Gunnedah were probably not entirely submerged beneath the waters of the Greta lake and may even have been undergoing some erosion.

Tertiary Igneous Rocks.

The Tertiary igneous rocks comprise the alkaline intrusives referred to above under the Boggabri Volcanics, together with some occurrences of dolerite and basalt.

The alkaline intrusives comprise rhyolites, trachytes, trachyandesites, andesites and pitchstones. They appear to be confined almost entirely to the area within which the Lower Marine flows outcrop and were probably intruded into a zone of weakness along a structural high. Jensen (1907) referred to acid igneous rocks intruding the Permian in the neighbourhood of Boggabri and it was probably in connection with these later igneous rocks that he noticed the evidence of their intrusive nature. This is well shown in portion 28, Parish of Leard, where rhyolite can be seen intruding *Glossopteris*-bearing shales which form part of the Wean formation.

The dolerites and basalts form only restricted outcrops, the main occurrences being on Mount Goonbri and between Maules and Back Creeks. The basalt outcrops shown on Yarrari Mount and Round Hill are taken from the map by Lloyd (1933). There is a small outcrop of amygdaloidal basalt in portion 13, Parish of Bollol, adjacent to the fault which forms the boundary between the Carboniferous and the Permian. Bores sunk through the alluvium in the vicinity of the northerly continuation of the line of the fault have also struck basalt.

Tertiary to Recent.

Sedimentary deposits of these ages are represented almost entirely by the alluvium of the Namoi River and its tributaries and occupy a large part of the area mapped. It is of the "black soil" type and in places it is many miles in width. Over portion of the area it may be underlain by Werrie Basalts which fail to outcrop because of the relative ease with which they weather.

STRUCTURAL GEOLOGY.

A large proportion of the region is obscured by alluvium and throughout much of the lower lying part of the area occupied by the Nandewar Group it is not possible to measure dips in the beds. However, such dips as were measured indicate that the central and western zones of the Nandewar Group form simple structures and have low dips or are lying almost horizontally. On the other hand, the eastern zone near the junction with the Carboniferous rocks is folded into a tight syncline, dips varying between 55° and almost 90° . The axis of the syncline trends north-north-west, parallel to the Carboniferous boundary. There is no doubt that this boundary is in the nature of a faulted junction. The tight folding and the dragging up of the beds of the Nandewar Group west of the fault until they are dipping almost vertically favour classifying the fault as a thrust. Lloyd (1933) mapped a fault further to the east which the writer considers to be a thrust. This means that north of the Namoi River there are two parallel thrust faults only a few miles apart, the same conditions as Carey (1934) found south of the Namoi River in the Werrie Basin. The fault mapped by Lloyd (1933) is probably the northerly continuation of Carey's eastern thrust and the one referred to above a continuation of his western thrust. Carey shows his eastern and western thrusts joining in the Babbinsboon area. It seems likely that the western thrust bifurcates near where it is met by the Babbinsboon fault, the main branch paralleling the portion of the eastern thrust which strikes nearly east and west and then swinging away more to the north, the other branch joining the eastern thrust as mapped by Carey.

Whether there is further faulting west of the western thrust it is not possible to say owing to the widespread alluvium, the lack of outcrops showing measurable dips and the absence of key horizons which can be mapped in the central and western zones.

The position of the synclinal area occupied by the Nandewar Group has been determined by the position of the original trough formed in Greta time. West of this trough the Lower Marine lava flows occur along what was probably a structural high even as early as that time. On the western side of the Namoi River the Greta sediments are either not developed or else occupy very restricted and isolated basins. At most points the Lower Marine lava flows are directly overlain by either Upper Marine or Upper Coal Measures sediments.

ACKNOWLEDGEMENTS.

I was assisted on this survey by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Dr. H. B. Walkom, Director of the Australian Museum, for the determinations of the fossil plants, and to Mr. H. F. Whitworth, M.Sc., Curator of the Mining Museum, for the petrological determinations. I also wish to express my thanks to Mr. J. E. Lancaster, Under-Secretary for Mines, and Mr. C. St. J. Mulholland, Government Geologist, for permission to publish this paper.

SUMMARY.

The area comprises a synclinal zone of Lower Coal Measures bounded on the west by Lower Marine lavas, which form a structural high, and on the other side

by Upper Kuttung (Carboniferous) rocks, which have been overthrust from the east. The Lower Marine lavas, and in part the Lower Coal Measures, have been intruded by a group of Tertiary alkaline rocks.

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PART IV

SYNTHESIS OF DITHIOHEXESTROL DIMETHYL ETHER.

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The remarkable estrogenic activity of the synthetic sex hormones stilbestrol, hexestrol and dienestrol discovered by Campbell, Dodds and Lawson (1938-9) and Dodds, Goldberg, Lawson and Robinson (1938-9) has resulted in the preparation and testing of many similar types of compounds. Investigations in these laboratories have been aimed at producing the sulphur analogues of some of these synthetic hormones and this paper reports the preparation of dithiohexestrol dimethyl ether.

The estrogenic activity of this ether is negligible; this may be connected with the difficulty of demethylation. Hexestrol dimethyl ether was found difficult to demethylate by Dodds, Goldberg, Lawson and Robinson (1939) and the sulphur analogue is even more resistant. Hydriodic acid, pyridine hydrochloride, potassium hydroxide and the method of Schonberg and Moubasher (1944) using magnesium iodide have no effect on dithiohexestrol dimethyl ether or thioanisole. Sodium in liquid ammonia demethylates thioanisole readily but no crystalline product could be isolated in preliminary experiments with dithiohexestrol dimethyl ether. Using the same technique anisole gave a very poor yield of phenol as previously shown by Birch (1947). The stability of methyl thioether groups to disruption has also been noted by Hodgson, Sibbald and Smith (1947).

The original scheme for the synthesis of dithiostilbestrol, involved the preparation of the alcohol, 1-(*p*-methylmercaptophenyl)-propanol-I, by reduction of *p*-methylmercaptopropiophenone. Many attempts to isolate the alcohol from the reduction products were unsuccessful, presumably due to the great ease of dehydration to *thioanethole*, which was obtained in one of these experiments. This hydrocarbon was then used to prepare dithiohexestrol dimethyl ether, by the method of Kharasch and Kleiman (1943) in twelve per cent. yield. Only one isomer was obtained in a pure form.

EXPERIMENTAL.

Thioanisole.

Thiophenol (400 g.) was dissolved in a solution of caustic soda (160 g.) in water (2 litres) contained in a three-necked flask fitted with a stirrer. Dimethyl sulphate (510 g.) was added with stirring and cooling. When the addition was complete the mixture was refluxed for one hour and the oil separated. The aqueous layer was extracted with ether and the oil and extracts dried over calcium chloride. The solvent was removed (thioanisole is appreciably volatile in ether), and the thioanisole distilled at 192-8° C. yield 425 g. (98%).

p-Methylmercaptopropiophenone.

Finely powdered anhydrous aluminium chloride (1.1 mol.) was placed in a three-necked flask fitted with reflux condenser, stirrer and dropping funnel and cooled in ice. Carbon disulphide (400 mls.) was added and then propionyl chloride (1.2 mol.) gradually added, with stirring, to the mixture, followed by the slow addition of thioanisole (1 mol.). The viscous mixture was stirred for one hour at room temperature and finally refluxed for ten minutes. The carbon disulphide

layer was then decanted and the green residue decomposed with ice and hydrochloric acid and ether extracted. The extract was washed with water and dried over calcium chloride. The solvent was removed and the ketone distilled under reduced pressure (b.p. 184° at 20 mm. approx.). The pale yellow solid (crude yield 92%) after one recrystallization from alcohol melted at 60–61° C. (82% recovery). Fractional concentration of the mother liquors gave no ortho compound. The pure ketone is a white crystalline solid, readily soluble in ether, alcohol and benzene, m.p. 61° C.

Found: C, 65.96; H, 6.54%; $C_{10}H_{12}OS$ requires C, 66.6, H, 6.6%.

The phenylhydrazone, oxime and semicarbazone of the ketone I were prepared in the usual manner, and the results are given in the table, together with the constants obtained for the sulphoxide and sulphone prepared by the methods of Gazdar and Smiles (1908) and Bost, Turner and Norton (1932).

TABLE I.

Compound	Formula.	Yield.	M.p.	Analysis.			
				Found.		Formula Requires.	
Phenylhydrazone ..	$C_{16}H_{18}N_2S$	100%	83–86°	N, 10.42		10.37	
Oxime ..	$C_{10}H_{12}ONS$		101°	N, 7.02		7.2	
Semicarbazone ..	$C_{11}H_{15}ON_3S$		162°	N, 16.8		17.7	
				C.	H.	C.	H.
Sulphoxide ..	$C_{10}H_{12}O_2S$	94%	96°	60.88	6.09	61.16	6.16
Sulphone ..	$C_{10}H_{12}O_3S$	58%	108°	56.25	5.67	56.55	5.7

The position of the propionyl group was indicated by alkaline cleavage of the 1-(α -methyl p-methylmercapto-phenacyl) pyridinium iodide, formed from the ketone by treatment with pyridine and iodine by the method of King, McWhirter and Rowland (1944), to the known p-methylmercapto-benzoic acid, m.p. 191° (Lit. 192°).

Preparation of Thioanethole. Reduction with Aluminium Isopropylate.

The Meerwein Ponderoff Verley method of reduction described by Wilds (1944) was successful in reducing the ketone to the alcohol, though attempts to isolate the alcohol failed. However, dehydration of the crude reaction product with potassium bisulphate gave thioanethole III, in 85% yield. Unpurified aluminium isopropylate was used in these reductions and was prepared in the usual way, using 1 g. aluminium foil for each 10 g. of ketone, together with 20 ml. dry isopropyl alcohol, 0.05 g. mercuric chloride and 0.2 cc. carbon tetrachloride. An equal volume of dry isopropyl alcohol was added to the solution of aluminium isopropylate when the ketone was added. After refluxing the mixture for ten minutes the slow distillation of acetone was carried out as described by Wilds (1944). When the dinitrophenylhydrazine test of the distillate was negative, the excess isopropyl alcohol was removed under reduced pressure and the residue hydrolysed by cold dilute hydrochloric acid (2 N). The mixture was extracted with ether, washed with water, and dried over anhydrous sodium sulphate. After removal of the ether the residue was heated with as much finely divided potassium bisulphate as there was ketone, originally, for 30 minutes at 180–190° C. After cooling, the mixture was extracted with ether and removal of the solvent followed by distillation under reduced pressure gave thioanethole III, a white solid, b.p. 143° C., at 25 mm. approx. Repeated recrystallization from methanol gave a white crystalline solid, m.p. 35° C.

Found: C, 72.9; H, 7.35%. $C_{10}H_{12}S$ requires C, 73.1; H, 7.36%.

The yield of thioanethole was 85%, the product had a distinct aniseed odour and instantly decolorized bromine in carbon tetrachloride.

Note.—If the oil is distilled in a stream of nitrogen before heating with potassium bisulphate, oils are obtained which give no ester derivatives with acid chlorides and which contain small amounts only of thioanethole. Distillation under reduced pressure with an air leak increased the amount of thioanethole.

Hexestrol Dimethyl Ether.

The thioanethole (1 mol.) was converted to the hydrobromide at -80°C . and then added to phenyl magnesium bromide and anhydrous cobalt chloride at -20°C . as described by Kharasch and Kleiman (1943). After stirring for a few hours the reaction mixture was poured into ice and acidified. Separation of the organic layer was followed by extraction with benzene. The organic extracts were dried with calcium chloride and after removal of the solvents the diphenyl formed in the reaction was removed by distillation under reduced pressure. The residue distilled at higher temperatures and no separation of fractions was made (b.p. $200-300^{\circ}\text{C}$. at 25 mm. approx.). The weight of crude product was 11.45 g. and recrystallization from ethyl alcohol to constant melting point gave 1.9 g. (12%) dithiohexestrol dimethyl ether m.p. 153°C .

Found: C, 72.46; H, 7.90%. $\text{C}_{20}\text{H}_{28}\text{S}_2$ requires C, 72.64; H, 7.94%.

Concentration of the mother liquors gave a yellow oil which, with ether, gave a small amount of a white solid, m.p. $133-136^{\circ}\text{C}$. There was insufficient to identify this substance.

Demethylation of Thioanisole.

The thioanisole (0.1 mole) was suspended in liquid ammonia (250 ml.) contained in a bolt-necked flask and small pieces of sodium (0.1 mole) were added with mechanical stirring till the characteristic blue colour was permanent. Solid ammonium chloride (11 g.) was added to decompose the sodium compounds and the ammonia evaporated on the water bath. The residue was acidified, extracted with ether, the ether extract shaken with aqueous caustic soda followed by acidification and extraction of the caustic soda solution with ether. After removal of the solvent the thiophenol was distilled, b.p. $168-170^{\circ}$. Yield 8 g. (73%). Diphenyl disulphide was also obtained by evaporation of the ether solution after it had been extracted with caustic soda solution. This is presumably formed by oxidation of the thiophenol during its extraction.

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SOME EFFECTS OF COMPRESSION ON THE PHYSICAL PROPERTIES OF LOW-RANK COAL.

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INTRODUCTION.

Irreversible changes accompanying air-drying of some Australian lignites were described in a recent paper (Dulhunty, 1946). The lignites were woody homogeneous materials, believed to be the precursor of vitrain, occurring in seams of brown coal. In the fresh moist condition they were soft and dull. After removal of water by air-drying, they became hard and brittle with the fracture and lustre of vitrain in sub-bituminous coal. The changes were found to be permanent as the lignites did not return to the soft dull condition when re-saturated with water. It was concluded that the lignites had reached a critical stage in rank advancement where the micelles were just touching with very small contact areas, and that the removal of water by air-drying allowed surface attraction to deform the micelles, reducing intervening spaces, and increasing contact areas and cohesive forces. This change in structure was believed to be responsible for development of hardness and bright lustre, and to account for the irreversible nature of the physical changes on the assumption that the internal pressure of adsorbed water, on re-saturating, was insufficient to overcome the increased cohesive forces.

Results recorded in this paper provide experimental evidence which supports the foregoing theory, and throw some light on the mechanism of physical rank advancement during natural metamorphism of coal.

NATURE OF PROBLEM AND OBJECTS OF EXPERIMENTS.

The changes described above were observed in lignites from Kiandra and Berridale in New South Wales, and from Yallourn in Victoria. More recent observations in Australia, Europe and America suggest that all brown coal seams pass through a critical stage in rank advancement during which the woody components, destined to become vitrain, exhibit permanent changes in hardness and lustre on air-drying. This may be described as the *high-rank brown-coal* stage at which the woody material is almost black, but soft and dull, with a maximum inherent moisture content of 65 to 80% (dry coal basis), a carbon content of 65% to 70% and a volatile yield of 40% to 50% (ash-free dry basis). It is regarded as a critical stage in rank advancement as the material appears to be ready to change to hard bright vitrain if natural metamorphism continues. This transformation, which takes place under water-saturated conditions in the earth's crust, is accompanied by reduction in maximum inherent moisture from the vicinity of 75% to about 25%. The changes are permanent as vitrain of sub-bituminous coal does not return to the soft dull condition when overlying strata are removed by mining operations or erosion.

The physical changes accompanying air-drying of woody lignite are similar in character to those which take place as a result of natural metamorphism or rank advancement, and it appears probable that modification of micelle structure

may be similar in each case. If this is so, the changes in structure on air-drying would be due to operation of attractive forces between the micelles when water is removed by evaporation, and in the case of natural metamorphism it would take place when pressure from overlying strata together with the forces of surface attraction exceed the internal pressure of adsorbed water. In view of this it appeared that it might be possible to induce permanent physical changes in hardness, moisture and lustre of lignite, without air-drying, as in the process of natural metamorphism, by application of an external compressional force which, added to the attractive forces between the micelles, exceeded the internal pressure of water adsorbed in inter-micelle spaces, if time of application was sufficient to allow deformation of the micelles and expulsion of water. With this object in view experiments were designed to reproduce, in the laboratory, conditions of temperature and compression, under water, similar to those in natural metamorphism, in an attempt to bring about permanent physical changes or advancement of physical rank.

APPARATUS AND EXPERIMENTAL TECHNIQUE.

Apparatus consisted of a press (illustrated in figure 1) designed to compress lignite and maintain compression during contraction of the material while immersed in a water bath at temperatures up to 100° C., or enclosed in a pressure vessel at higher temperatures. The pressure vessel was that described in an earlier publication (Dulhanty, 1942).

The press was provided with a heavy spiral spring arranged so that its force, when screwed down, operated against plungers at both ends of a pressure cylinder containing lignite. The spring was of sufficient length to maintain at least 95% of its original force, during contraction of the lignite, between stages at which it was reset. In experimental work the spring was used to provide a force of one ton at about two-thirds full compression. Three pressure cylinders with diameters of $\frac{3}{4}$, $\frac{1}{2}$ and $\frac{3}{8}$ in. were used for the purpose of obtaining compressional forces of approximately 5,000, 11,000 and 22,000 lb. per sq. in. respectively from the spring pressure of one ton. According to calculations previously recorded (Dulhanty, 1944) these compressional forces would be equivalent to about 4,300, 9,500 and 19,000 feet of coal-measure strata respectively.

Lignite used for charging the pressure cylinders was in the form of rods cut at right angles to the bedding plane. This orientation was adopted so that compressional force would be applied in a direction similar to that in which weight of overlying strata had acted in the past, and would continue to act on the seam during subsequent metamorphism if coalification continued.

In each experiment the rod, cut from lignite in its original water-saturated condition, was turned down until it would just slide into the pressure cylinder, care being taken to keep the material wet. The cylinder was then immersed in water to exclude air; the lignite was inserted; and the two plungers were placed against the ends of the rod, which was moved to a central position in the cylinder. The portions of the plungers protruding at each end of the cylinder were measured accurately to obtain the length of the rod. The cylinder was then placed in the press; the spring was screwed down; and the press, charged with lignite under compression, was immersed in oxygen-free water and heated at the required temperature. At various intervals (see Table 3) the press was cooled down and removed from the water to measure contraction of the lignite, reset the spring, or remove test pieces of lignite for examination.

GENERAL EFFECTS OF COMPRESSION UNDER WATER.

Preliminary tests were carried out on woody lignite (from Berridale, N.S.W.), pieces of which became bright and hard on air-drying. A rod cut from the soft

dull material in its original water-saturated condition was pressed in a $\frac{1}{2}$ in. cylinder, under water, at 27° C. with a compressional force of 11,000 lb. per sq. in. for a period of seven days. After compression the lignite was somewhat harder and fresh fracture surfaces exhibited a faint silky sheen, but on soaking in water for 24 hours it returned to the original soft dull condition. The test was then repeated at a temperature of 100° C. When removed from the press the lignite was hard and brittle and exhibited a bright lustre when fractured, and it did not return to the soft dull condition when soaked in water for six months. As far

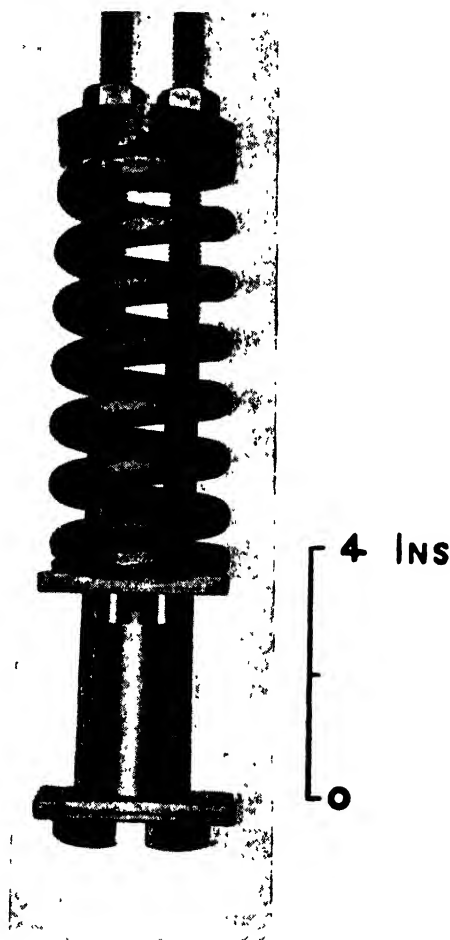


Fig. 1.

as could be judged by observation, the hardness and lustre were identical with those produced by air-drying, and the material could not be distinguished from the vitrain of sub-bituminous coal. Furthermore it did not crack, or break up when air-dried. No change in chemical properties, as a result of heating at 100° C. for seven days, could be detected by proximate and ultimate analyses carried out on the pressed material and control samples. During compression maximum inherent moisture was reduced from 76% to 24% and no increase took place after soaking in water for six months.

This experiment demonstrated the fact that irreversible changes in hardness, lustre and moisture content could be produced in lignite by application of

compressional force under water at temperatures, which although slightly elevated were too low to cause thermal decomposition over the period of heating.

A number of tests, employing conditions similar to those described above, was carried out on other pieces of woody lignite from Berridale, as well as pieces from Kiandra, Yallourn and Moorlands. Permanent physical changes were produced in all cases, but it was found, in general, that two kinds of lustre and structure were developed in different pieces of lignite from the same occurrence. Some pieces developed bright resinous lustre and conchoidal fracture very similar to vitrain. Others assumed a silky sheen and fibrous structure somewhat resembling fusain. Close examination of the original materials revealed slight differences. Those which produced material resembling vitrain after compression were a little more homogeneous and less fibrous than those which gave rise to material like fusain. The differences, however, were ill defined and both were soft and dull with the typical macroscopic grain-structure of wood, but after compression the two kinds of lustre and structure were quite distinct. The production of material resembling vitrain could be obtained by air-drying, but the fusain structure could not be produced as satisfactorily as by compression.

The foregoing observations suggest that differentiation of wood into the precursors of vitrain and fusain had taken place in the lignite at advanced brown-coal rank, although there was very little difference in superficial appearance. Application of compressional force to these materials appears to induce physical changes similar to the natural transformation of lignite to sub-bituminous coal, at which stage vitrain and fusain assume their separate physical identities. It also appears as though physical rank can be advanced to some extent without change in chemical rank, as no changes in proximate and ultimate composition took place during compression in the laboratory tests.

In experiments already referred to, and in those to be described later, removal of lignite rods from the cylinders was facilitated by an interesting phenomenon which followed release of spring pressure. Under pressure the lignite rod is pressed hard against the wall of the cylinder. Immediately after release of pressure the diameter of the rod decreases, and its length increases sufficiently to allow it to slide freely up and down the cylinder. After about 20 minutes, however, the diameter commences to increase again and the length decreases, with the result that the rod becomes tight in the cylinder and considerable force is necessary to move it from one position to another. Removal of rods could be effected with ease during the interval of 20 minutes following release of spring pressure. The dimensions of the changes were very small, probably less than 0.5%, but they were sufficient first to allow the rod to slide freely, and then to cause it to become tightly held in the cylinder.

RELATIVE INFLUENCE OF TIME, TEMPERATURE AND PRESSURE.

Additional experiments were carried out to obtain qualitative evidence of the relative influence of time, temperature and pressure in the development of permanent physical changes.

A large piece of Berridale lignite, possessing the properties summarized in Table 1, was selected for the experiments. It was soft, dull, and relatively homogeneous, although the original grain-structure of the wood was evident, and the material showed a distinct tendency to split along the grain as in normal wood. When dried in air it became hard and bright, and the fracture (essentially conchoidal) showed very little relation to the original grain-structure, or to the bedding plane of the seam in which it was embedded.

Six experiments were carried out under different conditions of time, temperature and pressure, as indicated in Table 2. At various intervals during each experiment contraction of the lignite was measured and a small test piece

TABLE I.
Properties of Berridale Lignite.

Maximum inherent moisture (dry basis)	79.52%
Proximate analysis (A.F.D. basis)—					
Volatiles	53.17
Fixed carbon	46.83
Ash (dry basis)	1.49
Ultimate analysis (A.F.D. basis)—					
Carbon	69.05
Hydrogen	5.29
Oxygen, nitrogen and sulphur	25.66

Geological age: Tertiary.

For nature of occurrence, see Dulhunty (1946).

was removed from the press to determine the extent to which permanent changes had developed. This was done by moving the lignite rod until the required amount protruded from the cylinder, and then cutting off the protruding portion so that the remaining section of the rod presented a flat face to the plunger when the press was reassembled. Immediately after removal from the press, each test piece was fractured to examine hardness and lustre. The broken pieces were then placed in water for four days to test the permanency of the physical changes. A period of four days was found to be sufficient to allow the lignite to reach stability. Some pieces were allowed to remain in water for as long as six months, but no further changes were detected. After soaking in water for four days, the pieces were again fractured to detect any reduction in lustre and hardness, and then maximum inherent moisture was determined.

Results of the experiments are summarized in Table 3. In experiment 1 the changes were complete and permanent, with a reduction in maximum inherent moisture to 24.8%, and it is evident that the conditions of time, temperature and pressure were greater than necessary to effect the changes. In experiment 2 the changes were almost complete at stage 1 with reduction in moisture to 37.4%, and complete at stage 2, where moisture reached 23.2%. Experiment 3 demonstrates the gradual development of physical changes and reduction of moisture to 24.7% at stage 4, where the changes became permanent. In experiment 4, the conditions were such that the changes were still incomplete at stage 5, after 153 days, when moisture had been reduced to 45.8% and the rate of change in physical properties had become extremely slow. The changes proceeded further in experiments 5 and 6, and moisture was reduced to about 36%, but the time in each case was insufficient to effect complete and permanent changes.

TABLE 2.
Experimental Conditions.

Experiment.	Diameter of Cylinder. (Inches.)	Compressional Force. (Lb. per sq. in.)	Temperature. (° C.)	Time. (Days.)	Gas Pressure on Water. (Ats.)
1	$\frac{1}{4}$	5,000	125	7	10
2	$\frac{1}{4}$	5,000	100	16	5
3	$\frac{1}{4}$	5,000	70	48	3
4	$\frac{1}{4}$	5,000	25	153	1
5	$\frac{1}{4}$	11,000	25	139	1
6	$\frac{1}{4}$	22,000	25	87	1

TABLE 3.
Results of Compression of Lignite.

Exp. No.	Stage No.	Time. (Days.)	Contraction. (% Orig. Vol.)	Max. Inh. Moist.	Properties after Compression.		Effect of Standing in Water for Four Days.
					Lustre.	Hardness.	
1	1	7	37.1	24.8	Very bright.	Hard, brittle.	No change.
2	1	1	32.29	37.4	Bright.	Hard.	Slight reduction in lustre and hardness.
	2	4	37.3	23.2	Very bright.	Hard, brittle.	No change.
	3	16	40.65	20.9	Very bright.	Hard, brittle.	No change.
3	1	2	32.1	51.8	Medium, bright.	Medium, hard.	Returned to soft dull condition.
	2	6	34.26	45.8	Bright.	Hard.	Returned to medium bright and medium hard.
	3	20	36.59	35.0	Bright.	Hard, medium brittle.	Slight reduction in lustre and hardness.
	4	48	38.03	24.7	Very bright.	Hard, brittle.	No change.
4	1	2	24.15	57.8	Dull.	Soft.	Remained dull and soft.
	2	6	30.57	52.2	Dull.	Soft.	Remained dull and soft.
	3	23	33.45	50.2	Faint bright.	Medium hard.	Returned to dull soft condition.
	4	51	35.45	48.7	Medium bright.	Medium hard.	Returned to dull soft condition.
	5	153	37.95	45.8	Bright.	Hard.	Returned to medium bright and medium hard
5	1	19	32.3	55.0	Bright.	Hard.	Returned almost to original condition.
	2	52	36.98	42.6	Bright.	Hard.	Returned to medium bright and medium hard.
	3	139	41.66	36.9	Very bright.	Hard.	Slight reduction in lustre and hardness.
6	1	2	26.35	48.0	Dull.	Soft.	Remained dull and soft.
	2	17	34.7	40.0	Medium bright.	Medium hard.	Returned almost to original condition.
	3	51	41.45	37.2	Bright.	Hard.	Returned to medium bright and medium hard.
	4	87	44.95	36.4	Very bright.	Hard, brittle.	Slight reduction in lustre and hardness.

The following conclusions may be drawn from the results :

(1) Both rate and extent of change in physical properties are functions of time, temperature and compressional force, and each factor operates as an independent variable.

(2) Under any given conditions of temperature and compressional force, rate of change becomes progressively slower with increasing time.

(3) Under certain conditions of temperature and compressional force (as in experiment 4) the rate of change may become infinitely slow before complete and permanent changes are effected, but with infinite time, which in relation to laboratory conditions is equivalent to geological time, the changes would eventually take place.

(4) With rise in temperature, the rate of change in physical properties increases very rapidly. This is evident from results of experiments 2, 3 and 4, in which a given compressional force of 5,000 lb. per sq. in. produced permanent changes in four days at 100° C., and in 48 days at 70° C., while at 25° C. it appeared that almost infinite time would be required. Similarly, the force of 5,000 lb. reduced moisture from 80% to 45% in less than one day at 100° C., in six days at 70° C., and in 153 days at 25° C.

(5) With increase in compressional force, the rate of change in physical properties increases rapidly. This can be seen from results of experiments 4, 5 and 6 (carried out at 25° C.) in which moisture was reduced to the vicinity of 45% in 153 days at 5,000 lb., in about 40 days at 11,000 lb., and in about three days at 22,000 lb.

(6) Under any conditions of temperature and compressional force, irreversible changes to the bright hard condition take place when moisture content is reduced to about 24%, and the volume of the material is reduced to about 40% of that which it occupied in the *high-rank brown-coal* stage.

(7) Progressive changes in lustre and hardness are reversible (on release of spring-pressure) until a critical stage is reached, after which they become irreversible. This is believed to be the stage at which the inter-micelle contact areas become sufficiently large to provide cohesive forces greater than the internal pressure of adsorbed water.

(8) Naturally occurring vitrain, in sub-bituminous coal, is permanently bright, hard and brittle, and it has a maximum inherent moisture content in the vicinity of 25%. As similar "vitrain", with comparable moisture content, was produced by compression of lignite, under water, at temperatures and pressures within limits normally expected at relatively shallow depths in the earth's crust, it is believed that the actual mechanism of natural metamorphism was reproduced in the laboratory and demonstrated by the results of experimental work.

Results recorded in this paper are essentially qualitative and of a preliminary nature. Improved apparatus and technique are at present being designed with the object of obtaining exact quantitative data regarding relations between time, temperature and pressure, and rate of change in physical properties, during the physical metamorphism of coal.

ACKNOWLEDGEMENTS.

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MINERALOGICAL EXAMINATION OF SOILS DEVELOPED ON THE PROSPECT HILL INTRUSION, NEW SOUTH WALES.*

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INTRODUCTION.

A soil survey of an area of 114 acres at Prospect Hill, N.S.W., was carried out in 1947 following its acquisition (Brewer, 1947) as the site for the new Sheep Biology Laboratory under the control of the Division of Animal Health and Production, C.S.I.R. It is situated 19 miles from Sydney on the Great Western Highway, and comprises two adjoining blocks, Portions 27 (part), 31, 32, 33, Parish of Prospect.

It was decided during the soil survey to attempt an investigation of the contamination of one soil parent material by another situated higher up the slope, by means of mineralogical analyses, and also to determine the usefulness of soil mineralogy as an aid in fixing soil boundaries where they are not obvious on the surface. Investigations were confined to the larger paddock surveyed (Fig. 1), which is situated on the eastern edge of the Prospect Hill intrusion and so affords the opportunity of studying the contaminating effects of a basic igneous rock situated on a rather steep hill above an area of Triassic sediments.

GEOLOGY AND TOPOGRAPHY.

The main topographic feature of the area is a moderately steep hill situated in the south-west corner and rising to a height of approximately 360 feet above sea-level. From this hill the country falls away rather sharply, the slope becoming progressively more gentle away from the hill down to the creek-lines around the base of the slopes at about 180 feet above sea-level. One of these creeks flows from west to east and is large enough to have built up narrow alluvial flats within the area being studied.

The chilled margin of the Prospect Hill intrusion forms the bed rock of the upper slopes of the hill. This intrusion is described (Jones *et al.*, 1911) as an

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essexite, the chilled margin of which resembles a basalt very closely in the hand specimen. The bed rock of the surrounding country is Triassic sediments into which the essexite has been intruded. These sediments consist of the Hawkesbury Series and the Wianamatta shale but, as there are no outcrops on the area it was not possible to determine which of these series forms the country rock. It is considered that the junction between the intruded rock and the surrounding Triassic sediments is quite steep and sharp (Jones *et al.*, 1911).

THE SOILS.

Detailed descriptions of the individual soil types can be obtained from the report on the soil survey (Brewer, 1947). In general the property consists of an area of Black Earths formed on the basaltic material of the chilled margin of the intrusion with podsolised types formed on the Triassic series on the lower slopes. A small area situated geographically between these two major soil groups was suspected as being of the Black Earth type over a substratum of light coloured clay formed on the Triassic series.

The true Black Earths consist of very dark brown to black, well-structured clays sometimes over browner clays which contain an accumulation of calcium carbonate in the form of concretions and sometimes (on top of the basaltic hill where the soils are rather shallow) directly over decomposed basaltic material into which they pass gradually. The podsolised types consist of greyish brown to brownish grey loams, silt loams, and silty clays, with some development of a bleached A_2 horizon, over variously coloured mottled clays sometimes with small accumulations of calcium carbonate in the B_2 horizon. The soils of the area between the Black Earths and the podsolised soils consist of dark coloured clay or silty clay over a browner clay containing some accumulations of calcium carbonate. This again overlies a light grey coloured clay which is not unlike some of the clays found under true Black Earths where they are residual soils. This clay is identical in appearance with the light coloured clays found under the podsolised soils where they were bored to sufficient depth.

In the survey of the unit discussed in this paper there is a complicated pattern of eight soil types, with three additional varieties or phases of those types (see Fig. 1). Of these soil types, T_2 and T_2A are of direct basaltic origin, and the remainder related to Triassic sediments as parent material.

SAMPLING.

Samples for mineralogical analyses were taken at varying intervals along two lines (see Fig. 1) from the top of the hill to the creek line at the bottom of the slope. Line I followed the southern boundary fence of the area, and the samples were taken at the following distances from the crest of the hill :

S_1 , 225 feet ; S_2 , 580 feet ; S_3 , 780 feet ; S_4 , 1050 feet ; S_5 , 1260 feet ; S_6 , 1450 feet.

In all cases the surface soil (0-6 inches) was taken and from S_2 onwards the subsoil was sampled from 24 to 30 inches. S_2 was sampled at a depth of 4 feet, at which depth the type of clay changed suddenly. S_1 was not sampled except for the surface soil because there appeared to be no significant change in the profile until the decomposed basaltic material was reached. The samples were taken with a hand auger, care being taken to prevent contamination of the samples, particularly in the sampling of the subsoils.

A similar procedure was followed for Line II, sampling from the creek line at the bottom of the slope up the slope to a small open quarry in the basaltic material. The intervals of sampling were :

S_7 , 0 feet ; S_8 , 200 feet ; S_9 , 460 feet ; S_{10} , 660 feet ; S_{11} , 895 feet ; S_{12} , 1145 feet.

In this case surface (0-6 inches) and subsoils (24-30 inches) were sampled at all sites.

For completeness and comparison the following miscellaneous samples were taken and examined :

S₁₃ : A sample of Triassic sandstone probably belonging to the Ostracod Beds, since it was calcareous. This outcropped on the Great Western Highway just outside the area.

S₁₄ : A sample of soil developed on shale occurring at the same location as S₁₃.

S₁₅ : A sample of the B₁ horizon of the black alluvial soil formed on the alluvial flats of the creek at the foot of the hill slope.

S₁₆ : The sample of the deep subsoil at 4 feet taken at site S₂ on Line I.

PREPARATION OF CONCENTRATES.

Investigations were confined to the fraction from 0.4 mm. to 0.02 mm., which includes the fine sand fraction and the finer end of the coarse sand fraction.

100 gm. lots of the air-dried samples were used for the concentration and separation of the heavy minerals. The soils were dispersed by means of an electric mixer with the aid of "calgon" as a dispersing agent. Twenty minutes' mixing was found to be sufficient for complete dispersion. Partial separation of the clay and silt was then obtained by the sedimentation process, which was carried out in 600 ml. beakers allowing the appropriate time for settling through 10 cm. at the prevailing temperature. The samples were then washed through a 0.4 mm. sieve with a stream of water from a wash-bottle. It was found that very little, if any, of the sample was held on the sieve, and this was discarded. Surface soils were then treated with 100 ml. of 10% hydrogen peroxide to remove organic matter. The separation of the fine sand fraction by sedimentation was then carried to its conclusion. All samples were then given successive treatments with 100 ml. of twice normal hydrochloric acid on a sand-bath at approximately 100° C. for 2 hours, until the liquid at the end of the treatment was almost colourless. This acid treatment removed iron oxide coatings from the grains. The acid was removed after each treatment and at the end of the treatments by washing with water, allowing to stand as for the sedimentation process, and decanting the supernatant liquid. The samples were then dried on the sand-bath and the fine sand was weighed.

10 gm. lots of the fine sand fractions were weighed out for separation by the heavy liquid method, bromoform of specific gravity 2.83 ± 0.01 being used. The separation was carried out in evaporating dishes.

The percentage of heavy minerals in the soil was calculated from the weight of heavy minerals recovered from 10 gm. of fine sand, the weight of total fine sand, and the weight of soil used for the separation. This almost certainly gives a low value, as the coarse silt and perhaps the coarser sand would contain some heavy residues. However, it is thought that, although these percentages are not strictly accurate, they can be compared one with another, since the same size-fraction has been used in all cases for the concentration of the heavy minerals.

The sandstone from the Triassic series was soft, calcareous and partially weathered, and complete disaggregation was obtained by careful crushing in an agate mortar. 100 gm. of this sample was then treated in the same way as the soil samples.

MICROSCOPIC EXAMINATION.

For purposes of identification of the mineral grains a small portion of the heavy concentrates was separated into strongly magnetic, magnetic and non-magnetic fractions by means of a bar magnet and a strong electromagnet. These

fractions were then separately mounted on gelatinised microslides following the method outlined by Marshall (1945). Where this separation was deemed unnecessary a single mount of the sample of the total heavy concentrate was made on the gelatinised microslides. Identifications were then made by the usual optical observations, and with the aid of a very limited range of refractive index liquids. For the optical observations clove oil ($RI \div 1.54$) was used on the gelatinised microslides as the immersion medium. A stream of acetone from a wash-bottle was used to remove the refractive index liquids after the determinations were made, and it was found that satisfactory permanent mounts could then be prepared by adding a small amount of Canada balsam to the gelatinised mounts, cooking for the requisite time, and then covering carefully with a coverslip.

Soils from sites S_1 , S_{13} , S_{14} , S_{15} and S_{16} were examined in detail. It was considered that S_{13} (the Triassic sandstone), S_{14} (the soil developed on shale), and S_1 (the surface soil of the Black Earth developed near the top of the basaltic rise) would represent the possible parent materials of the soils, i.e. the mineralogical assemblages would be close to those of the weathered sandstone, shale and basaltic material respectively. Since there were no outcrops of the Triassic series on the area, both the sandstone and the shale were considered.

The mineralogical analyses of these samples are given in Table 1. The remaining samples are not described in detail, but contain mixtures of varying proportions of the heavy minerals found in S_1 , S_{13} and S_{14} soil samples.

TABLE 1.

	Magnetite and Ilmenite.	Leucoxene.	Zircon.	Tourmaline.	Pyroxene (a).	Pyroxene (b).	Hornblende.	Rutile.	Garnet.	Monazite.	Anatase.	Riebeckite.	Phenaste.	Picotite.	% Heavy Concentrate in the Soil.
S_1 ..	A	R	VR		VA		+	+							12.9
S_{13}		F	O	C				R	+			?	?	?	0.06
S_{14}	R	VA	O	C		R		R		+					0.12
S_{15}	F	C	R	VR	R	VR		+		+	+	?			2.7
S_{16}	C	F	R	R			+	VR							0.11

F=flood => 70% of heavy concentrate.

VA=very abundant=50-70%.

A=abundant=30-50%.

C=common=10-30%.

O=occasional=5-10%.

R=rare=1-5%.

VR=very rare=0.1-1%.

+ =<0.1%.

?=doubtful identification.

DESCRIPTION AND DISTRIBUTION OF THE HEAVY MINERALS.

(1) *Zircon*. Is present as euhedral crystals, and worn and rounded grains. The shape of the crystals varies from short and stumpy, with terminal faces well developed, to tabular and, rarely, almost acicular with and without terminal faces. Inclusions are common and usually submicroscopic but sometimes larger and rod or tabular shaped, arranged parallel to the length of crystals. The mineral is colourless, but numerous minute inclusions sometimes give a cloudy grey appearance to the grains. Zoning was noted in some grains. The grains are dominantly at the lower end of the size fraction used. No particular concentration of any of the several varieties was noted in any one sample, all varieties seemingly occurring in all the samples examined.

(2) *Tourmaline*. Occurs in prismatic crystals rarely with poorly developed terminal faces, rounded worn grains and irregular grains. The colour and

pleochroism are very variable, grains occurring in varying shades of blues, browns, slate grey, buff and, rarely, green. Irregular colour zoning, especially in blues and browns, is fairly common, and this zoning occurs largely in the irregularly shaped grains. The grain-size is very variable. Again no particular occurrence of any of the several varieties is apparent, but tourmaline is absent from the basaltic material.

(3) *Rutile*. Is present in deep brown to yellow grains, often with good prismatic habit and sometimes rounded, irregular, or the typical bean-shape of worn grains. It shows the typical high adamantine lustre and appears to be largely primary, although compound grains of rutile and ilmenite were noted. Several of these compound grains appear to be a result of alteration of rutile to ilmenite rather than ilmenite to rutile. This is indicated by the fact that the ilmenite forms the borders and patches and fine streaks parallel to the length of the crystals, which are largely rutile and appear by their shape to belong to the tetragonal system. The grain-size is very variable. Rutile has a wide distribution, being present in all samples.

(4) *Pyroxene*. (a) The pyroxene of the basaltic material occurs in large irregular to subhedral prismatic crystals. It is purplish brown to neutral in colour and somewhat cloudy, with cleavage traces, very slight pleochroism and a large extinction angle, $Z \wedge c = 44^\circ$.

(b) The pyroxene of the sedimentary rocks occurs in clear, purplish grains with cleavage traces poorly developed. The grain-size is rather small. Pleochroism is very faint and the extinction angle is large. The grains are usually irregular in shape.

(5) *Leucoxene*. Is present in irregular and rounded grains as an alteration product after ilmenite. It occurs in varying amounts in all the samples examined. The grain-size is variable, but generally slightly towards the upper end of the size-fraction used.

(6) *Ilmenite*. Occurs in irregular grains of size about the middle of the size-fraction used. It is opaque, with a bluish grey lustre in reflected light, and generally shows alterations to leucoxene. It is present in most of the samples examined.

(7) *Magnetite*. Occurs very similarly to ilmenite, from which it is difficult to distinguish. It is silver grey in reflected light.

(8) *Garnet*. Occurs very rarely in the sample of Triassic sandstone. The grains are irregular and colourless with the typical rough surface. The grain-size is slightly towards the upper end of the size fraction used.

(9) *Hornblende*. Is present in the basaltic soil and in the deep subsoil at site S_2 , viz. (S_{16}). Its occurrence is very rare, there being only a few grains in each sample. It is green to brownish green in colour. The grain-size is about the middle of the size-fraction used.

(10) *Monazite*. Occurs in several samples as one or two rounded yellowish grains with the typical rough surface and high birefringence and relief. It was identified in the sample of soil on the shale (S_{14}) and the alluvial soil (S_{15}).

(11) *Riebeckite*. Occurs as irregular grains in the sample of Triassic sandstone (S_{13}) and the alluvial soil (S_{15}). It is in small, elongated, slightly fibrous grains, deep blue in colour and rather strongly pleochroic with a small extinction angle. It is very rare in occurrence.

(12) *Pleonaste*. Occurs as a single doubtful grain in the sample of Triassic sandstone (S_{13}). The grain is small, green and isotropic with high relief.

(13) *Picotite*. Has a similar occurrence to pleonaste. The grain is almost opaque, with brown translucent edges.

(14) *Anatase*. Is present as a few euhedral, square crystals of anthigenic origin in the sample of the alluvial soil (S_{15}). The grain-size is very small.

DETERMINATION OF SOIL BOUNDARIES.

A study of the heavy concentrates of the samples of Triassic sandstone (S_{13}), the soil developed on shale (S_{14}), and the basaltic material (S_1) showed a close similarity between the mineral assemblages of the sandstone and shale soils and a wide dissimilarity between these and the mineral assemblage of the basaltic material. The abundance of pyroxene in the basaltic assemblage and the significant zircon and tourmaline in the shale soils and the sandstone indicated that these three minerals could be used, together with the percentages of total heavy concentrates, to determine the origin of and the admixing of the parent materials of the area. Of these, the pyroxene, zircon and percentage of total heavy concentrate gave significant results in the attempt to determine soil boundaries by changes in mineral assemblages. Approximately quantitative estimates of these three units were obtained by the method of separation of the heavy concentrates and then by a count of about 1000 grains in each sample. These estimates were made on all the samples collected (both surfaces and subsoils) on Line 1 and Line 2 and are plotted as histograms (Figs. 2, 3). The profile of the land form has been drawn on each graph by plotting height above sea-level in feet against distance in feet from the south-west corner of the area for Line 1 and from site S_7 near the creek line for Line 2. The positions of the sampling sites have been marked on these profiles (Fig. 1).

Figure 2 deals with the surface soils and subsoils on Line 1 and shows, plotted against distance in feet from the south-west corner of the area (i.e. for the position of each sampling site) the percentage of pyroxene in the soil, the percentage of zircon in the soil and the ratios of $\frac{\text{percentage of pyroxene}}{\text{percentage of total heavy concentrate}}$ in the soil, and $\frac{\text{percentage of zircon}}{\text{percentage of total heavy concentrate}}$ in the soil. The percentage of heavy concentrate in the soil is also shown separately. The ratios were plotted to show that the percentage of total heavy concentrate in the soil was not the only significant factor.

Figure 3 deals with the surface soils and subsoils on Line 2. The profile of the landform and the percentage of total heavy concentrate and the percentage of zircon in the soil have been plotted for both the surface soils and the subsoils. The percentage of pyroxene in the soil has also been plotted for the surface soils.

DISCUSSION.

A study of the histograms shows several sharp breaks in the mineralogical constitution of the soils, and these breaks correspond to soil boundaries.

The histograms for the surface soils of Line 1 show a major break in parent material occurring between S_3 and S_4 and probably centred about a point 1000 feet from the south-west corner of the area. This break is shown on the histogram by a sudden fall in the percentage of pyroxene followed by a flattening off, by a sudden rise in the percentage of zircon, by a very sudden fall in the ratio of percentage of pyroxene to percentage of heavy concentrate and by a very sudden rise in the ratio of percentage of zircon to percentage of heavy concentrate. The total heavy concentrate histograms also show a sharp fall to a point beyond S_3 with a gradual fall from that point to the foot of the hill slope.

The histograms for the subsoil sample of Line 1 show practically no change in the amount of zircon over the whole line except for an increase between S_2 and S_3 coming down the line. On the other hand the pyroxene shows a steady but very slight increase from the lower slopes up to the subsoil at S_2 , where

it rises very sharply. At S_1 the boring went straight on to decomposed basalt, so the subsoil has been taken as having the same mineral assemblage as the surface soil. Thus between S_2 and S_3 there is a sudden change in the parentage of the subsoil material.

From this it can be deduced that the subsoils of the podsolised soils have a fairly uniform parentage which continues under S_3 and which is intermediate in

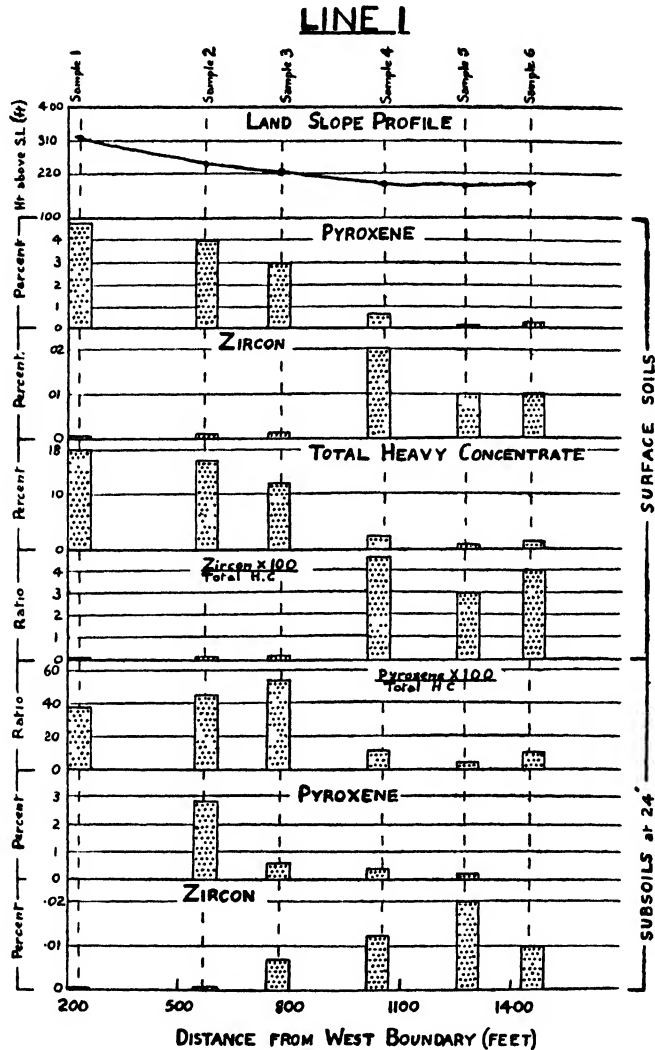


Fig. 2.

type between material derived from the basaltic chilled margin of the intrusion and the Triassic series. The percentage of total heavy concentrate in these subsoils also indicates uniform parentage.

From this discussion it can be said that there is evidence of two breaks in the origin of the parent materials of the soils based on the mineralogy of the surface soils and the subsoils of the profiles. These supply evidence of the existence of soil boundaries at the points where the changes occur, namely between S_2 and S_3 and between S_3 and S_4 . The first break is in the subsoil and indicates the presence of a double profile and the soil boundary between T_2 (Area A) and

T_2A (Fig. 1). The second break shows in the surface soils and indicates the existence of the soil boundary between T_2A and T_3 (Fig. 1). As can be seen from the soil map, these mineralogical results indicate that this latter soil boundary should be situated about 100 feet west of the boundary mapped during the soil survey. Further evidence of this latter soil boundary is found in the

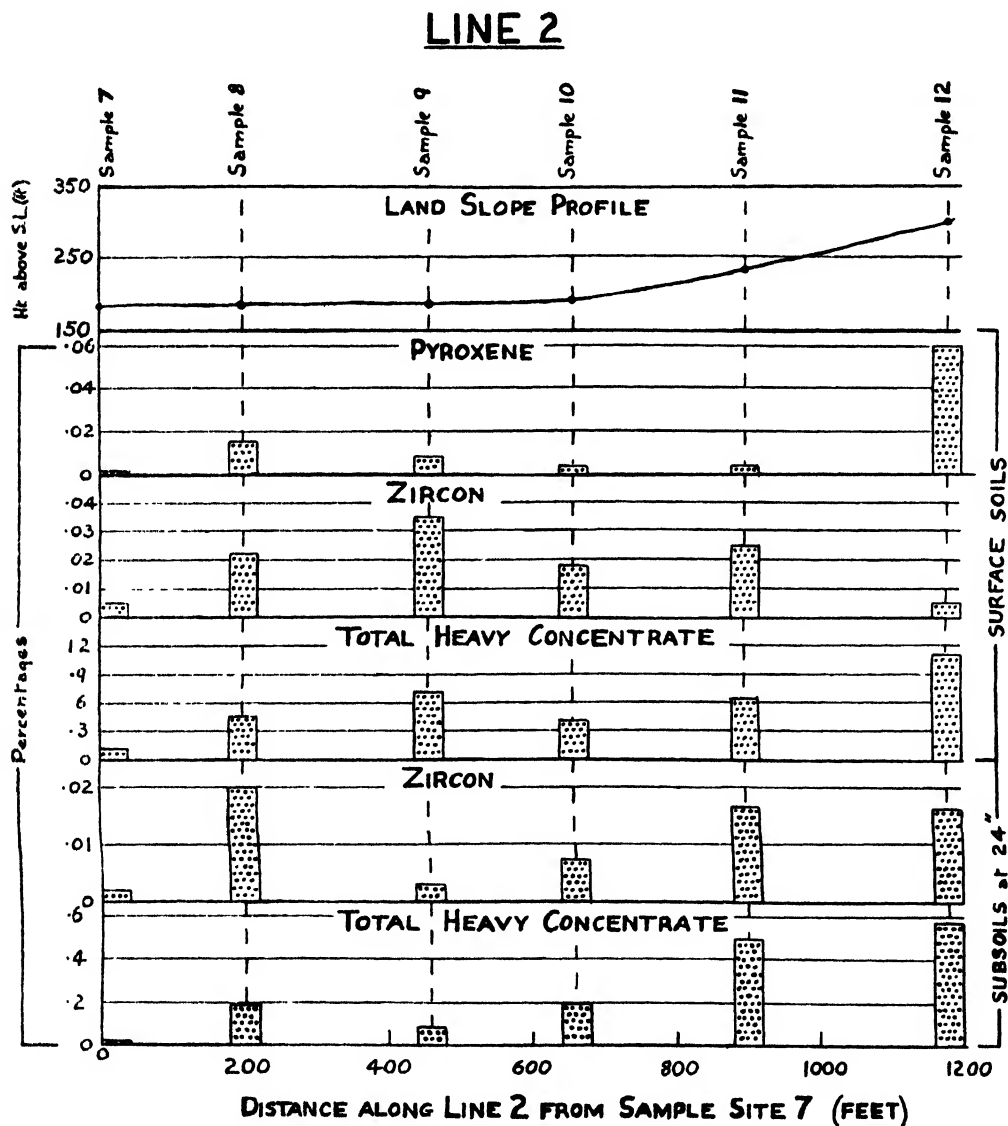


Fig. 3.

fact that tourmaline forms quite a significant member of the mineral assemblages in the samples from S_4 onward, whereas it is absent from the surface soils above this point.

The histograms for Line 2 do not show such marked breaks in the type of parent material as do those for Line 1. There is a general but uneven rise in the percentage of heavy concentrate in both the surface soils and subsoils from the creek line up the slope. The pyroxene of the surface soil rises quite sharply between S_{11} and S_{12} and this does indicate a break at the point where contamina-

tion from the basaltic material has sharply increased. The subsoils all along Line 2 have very little or none of the basaltic type of pyroxene and so are probably not contaminated by the basaltic material, the contamination along this line being confined to the surface soils in which it is generally small but increases up the slope. Also, the subsoils contain a fairly even distribution of zircon along the whole line, indicating uniformity of parent material. Lastly, all the subsoils and surface soils contain tourmaline as a significant member of their mineral assemblages.

A possible explanation of the lack of uniformity in the trends of the histograms for Line 2 is that the line traverses several different soil types which are fairly closely related to one another but whose soil-forming processes, and possibly parent materials, may be sufficiently different to cause variations in the mineral assemblages. Several minor breaks are indicated by the histograms for both the subsoils and the surface soils, but the samples were insufficient in number and too widely spaced to assess accurately the significance of these small variations in mineral assemblage. The histograms of pyroxene for the surface soils and zircon and total heavy concentrate for the subsoils indicate a minor break between S_6 and S_7 , which may possibly be explained by the influence of the creek at S_7 . The break between S_{11} and S_{12} is a significant one, and it can be said with certainty that a soil boundary does exist between S_{11} and S_{12} and probably close to S_{12} , since at that point pyroxene is still low compared with the percentage of pyroxene in the soils of mixed origin on Line 1. This boundary corresponds to the boundary between T_2 and T_1 (Fig. 1).

DETERMINATION OF THE ADMIXING OF PARENT MATERIALS AND CONTAMINATION BY SOIL CREEP.

It is evident from the mineralogical analyses that the podsolised soils have been developed from parent material of a different origin from that of Black Earths. The geology of the area has been studied (Jones *et al.*, 1911) and the obvious conclusion is that the major portion of the parent material of the podsolised types has not been derived from the basaltic chilled margin of the intrusion. The possible sources of parent material for the podsolised types are, therefore, the Hawkesbury series and the Wianamatta series. The samples of sandstone and soil developed on shale (S_{13} and S_{14}) studied above have been taken as the most likely sources of parent material for these soils, since both occur within a few chains of the area.

A consideration of the histograms of Fig. 2 for Line 1 brings out several facts. One is that both the subsoils and surface soils of the podsolised types show a percentage of total heavy concentrate much greater than that of either the Triassic sandstone or the soil developed on shale. The surface soil at S_6 at the foot of the slope has 2.7% of heavy concentrate, which is the lowest for the surface soils on Line 1. The shale soil has only 0.12% and the Triassic sandstone 0.06% of heavy concentrate. Thus it should be possible, by accurate measurements of the percentages of various mineral species in the parent materials, the soil concerned, and the contaminating material, to evaluate the percentage of contamination of one parent material by another; in this case of the parent material of the podsolised soil types (S_{13} and S_{14}) by the basaltic material from higher up the slope. A rough calculation based on the percentage of total heavy concentrate in the basaltic material, the soil developed on shale and the surface soil at S_6 showed a contamination of 20% of basaltic material in the surface soil of S_6 . A similar calculation based on the pyroxene typical of the basaltic material gave a contamination of 6%, while the soil developed on shale had approximately the same percentage of zircon as the surface soil at S_6 . Similar calculations for the subsoil at S_6 gave a contamination of 10% based on the total heavy concentrates and of 2% based on the pyroxene.

The variable results obtained from the above calculations indicate that several considerations have to be taken into account to obtain correct results. The first is the amount of weathering undergone by the pyroxene during the admixing and since then, due to soil-forming processes. This will reduce the amount of pyroxene now present as compared with the amount present in the contaminating material, and so the calculation based on the pyroxene is probably an underestimate. The second is the differential movement of grains of different specific gravity down the slope. Heavier minerals probably move more quickly than lighter ones and so contribute more to the contamination. The amount of this differential movement may or may not be significant. The third is the mean specific gravities of the various heavy concentrates. In the above calculations, based on the percentage of total heavy concentrate, the assumption was made that the mean specific gravity of all the heavy concentrates was the same. However, the contaminating minerals are probably largely the heavy opaques, so that the mean specific gravity has probably been underestimated, and therefore the percentage of contamination based on this method overestimated. The fourth is that the heavy liquid separations are not accurately quantitative, and this would especially upset any calculations based on the percentage of zircon, as it is present in relatively very small amounts.

The conclusions to be drawn from these considerations are that the method requires a series of quantitative separations to obtain accurately the percentage of heavy concentrate in each sample and to determine any differential movement of the various mineral species down the slope. The specific gravity of the contaminating and contaminated materials should be determined as accurately as possible. Calculations should be based on determinations made on a very resistant mineral such as zircon which is usually present in relatively small amounts, so adding to the necessity for quantitative separations. Further, it should be noted that, apart from any contaminating process, the soil-forming and weathering processes will result in a different percentage of all the heavy minerals in a soil than in the fresh unweathered rock, so that only weathered materials should be compared.

A further observation from the mineralogical analyses is that the surface soils of the podsolised types on Line 1 are richer in heavy minerals than the subsoils. The lowest heavy concentrate in the surface soils is 2.7% at S_6 . The subsoil at this position has 1.2% of heavy concentrate. This indicates that apart from the original intermixing of parent materials on which the podsolised soils were developed a further contamination of the surface soil has occurred by soil creep down the slope. This contamination is probably still continuing, maintaining or even increasing the percentage of heavy minerals in the surface soils, while the percentage in the subsoils may be decreasing due to weathering processes. Evidence of soil creep and decreasing contamination with increasing distance from the source of the contaminating material is also seen in the decreasing percentage of heavy concentrate in the surface soils of the podsolised types, with increasing distance down the slope in Line 1. However, the percentage of heavy concentrate in the surface soils is consistently greater than that in the subsoils. This may be explained partly by the greater leaching due to the weathering processes in the surface soils.

Thus it can be deduced that the parent material of the podsolised soils consists of a mixture of material derived from the Triassic series and material derived from the basaltic chilled margin of the Prospect intrusion and that soil creep has further enriched the surface soils with material derived from the latter source. The amount of basaltic material in the mixed parent material has been estimated by the methods used as from 2% to 10% for the original parent material and 6% to 20% for the surface soils at S_6 . The percentage for the surface soils increases up the slope.

The soil of the alluvial floodplain is very similar mineralogically to the surface soil at Site S₆ on Line 1. It has 2.7% of heavy concentrate, 4% of which is pyroxene derived from the basaltic material. It also contains a small amount of tourmaline derived from the Triassic series. The parent material therefore is again a mixture of Triassic material and basaltic material, but here the mixing is due to water action. The percentage contamination of the Triassic material by the basaltic material is probably the same as for the surface soil at S₆.

RECENT HISTORY OF THE AREA.

From these mineralogical considerations an attempt can be made to interpret the recent history of weathering along Line 1. The Prospect intrusion is known to have a steep contact with the Triassic series and to be intruded into that series (Jones *et al.*, 1911). Figure 4A gives some idea of the probable state of affairs immediately after intrusion. Denudation would then reduce the position to that shown in Fig. 4B. Further weathering and erosion would tend quickly to reduce the steep slope of the exposed chilled margin of the intrusion since this is basaltic in nature and so readily weatherable. The weathered basaltic material would spread itself down the slope, intermixing with the weathering Triassic series, giving rise to a state of affairs as in Fig. 4C, where there is an area of purely weathered basaltic material (A-A₁) beyond the boundary of the intrusion with the Triassic series. Below this occurs a mixture of basaltic material and Triassic debris (A'-A''). These are both underlain by the Triassic series. A-A'-A'' represents Line 1.

This interpretation is borne out by the mineralogical analyses. The hill crest consisted of Black Earths with heavy concentrate up to 13%, but decreasing down the slope as the depth of soil, and so the weathering effects increased (Fig. 2). Proceeding down the slope the area A-A' showed no sudden changes in mineral assemblage, but a gradual fall in percentage of heavy concentrate, and was underlain by a light grey clay with only 0.11% of heavy concentrate (S₁₆). At A' a sudden break in the histograms of Fig. 2 showed a change to the mixed Triassic and basaltic parent material.

Soils then developed on these parent materials when the hill slope had reached a stable condition. Further gradual erosion by the normal processes operating at the present time, principally soil creep, have resulted in an enrichment of the surface soils lower down the slope by basaltic material.

SUMMARY AND CONCLUSIONS

Soil samples were collected along two lines up a hill slope the top of which consisted of Black Earths developed on the chilled margin of an essexite intrusion and the lower slopes of podsolised soils developed on the Triassic series. Mineralogical analyses of the heavy concentrates of the surface and subsoils at two feet were made for these samples and the results plotted as two series of histograms together with the profile of the land form. For comparison, analyses were made of a Triassic sandstone, a soil developed on Triassic shale, the alluvial soil near a creek line at the foot of the slope and the deep subsoil below a Black Earth in the transition zone between the two types of parent material.

Examination of the resultant histograms showed several breaks in slope which indicated the presence of soil boundaries, definitely in the case of Line 1 but less obviously in the case of Line 2. Consideration of percentages of pyroxene and of heavy concentrate in the soils and in the samples from the Triassic series showed that the podsolised soils were developed on parent material of mixed origin and that the surface soils were being further contaminated by the process of soil creep. The alluvial soil was shown to be formed from similar mixed parent material. Quantitative estimates of the amount of mixing of parent materials were not possible because of the lack of precision in the methods used.

A general account of the recent history of weathering along Line 1 was deduced from the mineralogical studies in conjunction with the geological data available.

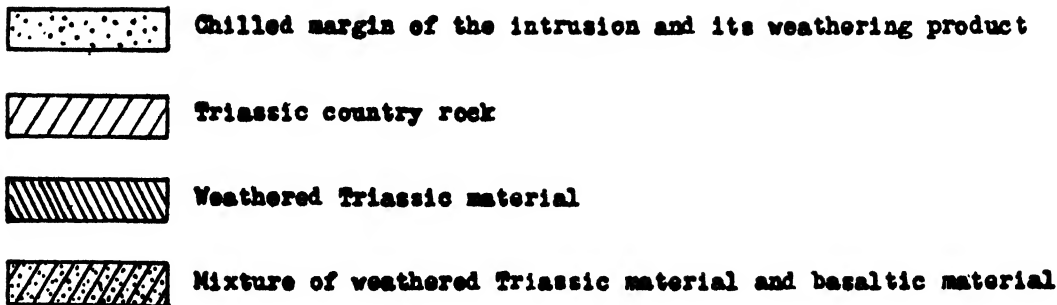
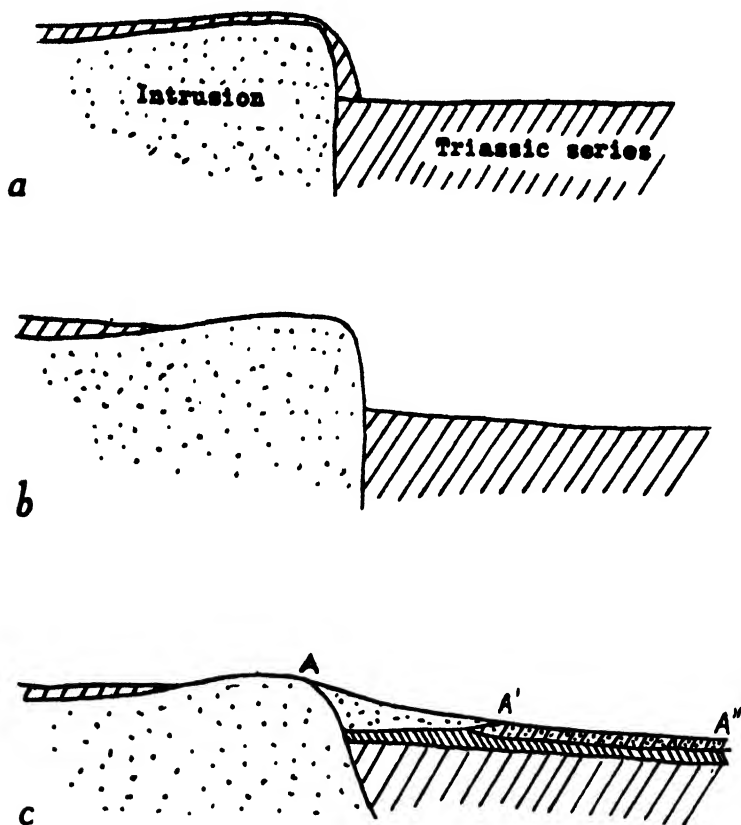


Fig. 4.—Illustrating the origin of soil material on the margin of the basaltic intrusion, Prospect Hill, N.S.W.

From these observations it has been concluded that mineralogical analyses can be used

- (1) to determine the position of soil boundaries where they may not be very evident on the surface ;
- (2) to determine the recent history of weathering which, in general, has been neglected by both geologists and pedologists ;

- (3) to determine qualitatively the admixing of parent materials ;
- (4) to determine quantitatively the approximate percentages of admixing of parent materials provided a quantitative method of separation is used and the calculations are based on the occurrence of a very resistant mineral such as zircon or tourmaline.

ACKNOWLEDGEMENTS.

Thanks are due to Mr. G. Cochrane, of the Division of Soils, C.S.I.R., for help in the collection and preparation of the samples, for suggestions on methods of presentation, and for reading the manuscript. Thanks are also due to Dr. Hallsworth, of the School of Agriculture, Sydney University, for his kindness in supplying laboratory accommodation and some of the equipment necessary ; to Mr. J. K. Taylor, Chief of the Division of Soils, C.S.I.R., for assistance in the preparation of the manuscript ; and to Dr. D. Carroll for reading the manuscript.

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RELATIONS OF RANK TO INHERENT MOISTURE OF VITRAIN AND PERMANENT MOISTURE REDUCTION ON DRYING.

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INTRODUCTION.

A definite relationship has been established between rank and moisture content for medium to high-rank coals (Dunningham, 1943; Gauger, 1932; King and Wilkins, 1943; Mott, 1943; Porter and Ralston, 1916; Rees, Reed and Lands, 1939). Moisture decreases with rank until about 88% carbon is reached, after which it increases again as rank becomes higher. Moisture varies within certain limits for coals of any particular carbon content, therefore the graphical relationship is of the nature of a zone within which coals fall when moisture is plotted against carbon. The zone is relatively narrow at about 88% carbon where moisture reaches a minimum, but it becomes wider as moisture increases towards both the anthracite and sub-bituminous rank-stages.

The well-defined minimum at the high-rank bituminous stage is regarded as an important feature in the moisture-rank relationship. It is at about this stage in rank advancement that coal attains its maximum caking and swelling properties, reaches a minimum in internal surface, develops marked anisotropism, and commences to show other chemical and physical changes which mark the first stages of anthracitization.

Results recorded for coals of rank lower than sub-bituminous show a very wide moisture-rank zone in the vicinity of the brown-coal stage, suggesting wide variation in moisture for any given carbon content when coals from different deposits are plotted on the same graph. In general, it has been inferred that moisture continues to increase as rank decreases from sub-bituminous coal, through the brown coals, to peat. This may be so if total bed-moisture is considered, because the texture of coal becomes increasingly open and spongy as the peat stage is approached, and the amount of adherent moisture which can be drained out by lifting it from the deposit, or squeezed out by pressing it in the hand, increases greatly. Such adherent moisture is merely lying in the bed and cannot be considered to bear any relation to the physical condition of the coal substance making up the individual fibres and pieces of plant material in the brown coal or peat.

Investigations described in this paper deal with the moisture actually adsorbed by the coal substance, and it is believed that results have established the existence of a maximum in the moisture-rank zone at about 67% carbon. The maximum appears to be well-defined, and it is probable that it corresponds with important changes in the development of micelle structure during rank advancement.

An investigation was also made of relations between rank and permanent changes in moisture content due to drying coals from their original water-saturated condition. Results of this work show that changes are greatest for coals with the highest inherent moisture contents, and that coals cease to undergo permanent changes after a certain rank-stage is reached.

RELATIONS OF MAXIMUM INHERENT MOISTURE TO RANK.

Materials used in this investigation consisted of vitrains separated by hand from lump-specimens of coal ranging in rank from semi-anthracite to sub-bituminous, and the woody precursors of vitrain in the case of lower rank coals. The general nature of the materials, and their chemical properties, are summarized in Table 1.

TABLE 1.
Results of Investigation of Moisture-Rank Relations.

Spec. No.	Locality.	Geol. Age.	Rank.	Chem. Props. (A.F.D. Basis.)		Max. Inher. Moist. % (A.F.D.)	Ash % (D.C.).
				% Carbon.	% Vol. Cont.		
208	Baralaba, Q'land ..	Perm.	Semi-Anthr.	91.6	10.6	3.22*	1.98
28	Mittagong, N.S.W. ..	Perm.	Semi-Anthr.	91.5	7.4	3.93*	5.74
161	York Plains, Tasmania	Trias.	Semi-Anthr.	90.3	11.7	4.06*	3.61
310	Greta Seam, Aberdare, N.S.W.	Perm.	High-rank bitumin.	89.2	39.5	4.00*	1.52
312 } 314 } 30 }	Bulli Seam, Coalcliff, N.S.W.	Perm.	High-rank Bitumin.	88.6	22.9	1.88	0.90
	Top Seam, Sydney, N.S.W.	Perm.	High-rank Bitumin.	88.3	23.5	3.21*	1.03
312	Bulli Seam, Helensburgh, N.S.W.	Perm.	High-rank Bitumin.	88.0	24.9	1.82*	0.81
460	Wallarrah Seam, Wallarah, N.S.W.	Perm.	Bitumin.	84.1	33.3	5.77	1.32
458	Victoria Tun. Sm., Red Head, N.S.W.	Perm.	Bitumin.	83.7	36.9	4.01	2.59
459	Gt. Northern Seam, Belmont, N.S.W.	Perm.	Bitumin.	83.4	37.6	4.81	1.79
288	Wonthaggi, Victoria ..	Jur.	Bitumin.	82.0	34.4	13.35	1.19
124	Mt. Nicholas, Tasmania	Trias.	Bitumin.	81.9	34.6	18.23*	0.38
169	Borehole Seam, Wallsend, N.S.W.	Perm.	Bitumin.	81.3	34.4	5.55*	2.09
174	Liddell Seam, Liddell, N.S.W.	Perm.	Bitumin.	81.0	40.9	4.03*	2.99
212	Mt. Mulligan, Q'land. ..	Perm.	Bitumin.	80.7	29.7	6.93*	1.58
138	Wonthaggi, Victoria ..	Jur.	Bitumin.	80.3	38.2	15.43*	1.04
186	Seymour, Tasmania ..	Trias.	Bitumin.	80.0	36.5	10.20*	2.66
461	Wallarrah Seam, Swansea, N.S.W.	Perm.	Bitumin.	79.8	36.3	6.10	6.45
143	Bluff Seam, Ipswich, Q'land.	Trias.	Bitumin.	79.1	35.5	4.53*	5.04
209	Callide, Q'land ..	Jur.	Bitumin.	77.9	36.8	21.45*	1.79
317	Griffin Seam, Collie, W. Aust.	Perm.	Sub-Bitumin.	76.6	32.9	26.20	2.38
120	Twelve Foot Seam, Collie, W. Aust.	Perm.	Sub-Bitumin.	74.8	34.7	26.00*	1.90
304	Leigh Creek, S. Aust. ..	Trias.	Sub-Bitumin.	74.5	36.2	67.50	3.83
457	Bovey Tracey, England	Tert.	Brown Coal.	70.5	54.4	61.45	1.87
456	Moosonee, Canada ..	Cret.	Brown Coal.	69.8	51.6	85.00	2.69
88	Berridale, N.S.W. ..	Tert.	Brown Coal.	68.9	53.8	78.82	3.20
454	Liblar, Germany ..	Tert.	Brown Coal.	68.3	54.7	94.60	1.39
136	Yallourn, Victoria ..	Tert.	Brown Coal.	67.4	60.1	118.30	1.79
455	Liblar, Germany ..	Tert.	Brown Coal.	62.5	64.6	69.30	1.79
104	Kiandra, N.S.W. ..	Tert.	Brown Coal.	59.2	76.4	61.30	0.43
453	Haltern, Germany ..	Pleis.	Peat.	58.2	87.7	38.75	0.31

* Values obtained by evacuation and resaturation of oven-dried vitrain.

The vitrains with carbon content higher than 74.5% were hard bright materials typical of normal vitrain. Those with less carbon were soft and dull with woody structure, and varied in colour from black to yellow-brown. Of these, the black materials containing approximately 68% to 74% carbon became hard and bright when dried, indicating that they were approaching the rank-stage at which soft dull woody lignite changes to hard bright vitrain under normal conditions of natural metamorphism (Dulhunty, 1946, 1948). The two pieces of woody lignite from the Cologne deposits in Germany (Nos. 454 and 455) were black and yellow-brown with carbon contents of 68.3% and 62.5% respectively. Materials, in Table 1, with 67.4% carbon and less were of yellow-brown colour, and although they became somewhat harder and more brittle on drying, they did not develop bright lustre.

Vitrains, and their woody precursors, were used so as to obtain results which would be comparable for coals containing different proportions of petrological constituents. This was considered essential as moisture contents vary considerably in the different banded constituents of coal.

Results described later in this paper indicate that vitrains containing less than 87% carbon undergo permanent reduction in maximum inherent moisture when dried, but those of higher rank are not affected in the same way and, if completely resaturated, will take up as much water as they held in their original saturated condition. As a result of this all vitrains with carbon content lower than 78%, used in the study of moisture-rank relationships, were materials which had been collected and maintained in their original water-saturated condition. In the case of coals of higher rank, some of the vitrains (marked with an asterisk in Table 1) were separated from specimens which had been allowed to air-dry as fresh water-saturated materials were not available, but after separation they were thoroughly evacuated and resaturated, by the method described later in this paper, before determining maximum inherent moisture.

Results for inherent moisture, carbon and volatiles are quoted as percentages of the dry ash-free vitrains. They were not recalculated according to any of the ash-correction formulas. The ash contents of materials with less than 77% carbon was so low, mainly between 1% and 2%, that the influence of mineral matter would be negligible. Vitrains with more than 77% carbon were saturated with water, then treated with a 5% solution of hydrochloric acid, and finally washed with water until acid-free. This removed mineral matter adhering to the vitrain particles, and reduced ash contents to between 1% and 3% in all except three cases where the ash contents were between 4% and 6% (see Table 1).

The values for moisture (Table 1) represent *maximum inherent moisture* determined by *controlled vaporization of adherent moisture* using the apparatus and technique described in an earlier publication (Dulhunty, 1947). Moisture contents determined in this way approximate very closely to absolute values for inherent moisture contained in all pores small enough to lower the vapour pressure of water, and which are considered to be part of the essential micelle structure of the coal substance. Adherent moisture with normal vapour pressure, contained in macroscopic cracks and openings, is removed during the process of determination. Values for maximum inherent moisture determined by this method are comparable for coals of all ranks and textures, and they are considered to be the most satisfactory for investigating relations between moisture and rank. Methods involving partial drying of coal, followed by resaturating in an atmosphere of water vapour under a pressure equal to the vapour pressure of water at the temperature employed, are not suitable as low rank coals undergo irreversible changes on drying. Results representing total moisture in the coal, as mined, are likely to be misleading owing to the presence of large amounts of adherent moisture in the case of some low-rank coals, and the fact that the

natural bed moisture may be less than the maximum inherent moisture, producing "dusty conditions" in underground mines, in the case of some high-rank coals. Dunningham's Blotting Paper Method (Dunningham, 1943) gives significant results, but the standard amount of drying must be varied for coals of different ranks and textures, and this introduces difficulties when inherent moistures are to be compared in coals ranging from peat to anthracite.

The foregoing procedure consisted of the use of low-rank coals in their original water-saturated condition to avoid changes due to drying; the separation of pure vitrain to avoid the influence of different proportions of petrological constituents; and the use of a method of moisture determination which eliminates adherent moisture without any preliminary drying effects. This was adopted with the object of obtaining moisture results closely related to the physical condition or rank of the coal substance.

Results for carbon content and maximum inherent moisture, listed in Table 1, were plotted graphically as shown in Fig. 1. Curves drawn

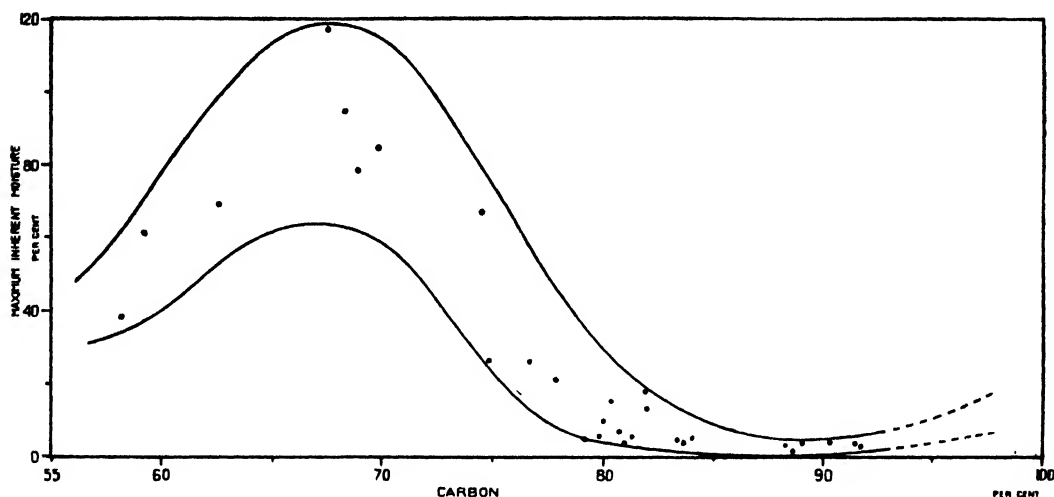


Fig. 1.—Diagram illustrating zonal relationship between maximum inherent moisture and rank of vitrain.

approximately at the upper and lower limits of the points, represent the zone within which the vitrains fall, or the zonal relationship between maximum inherent moisture and rank. The broken lines above 93% carbon, representing the extension of the zone into anthracite rank, are based on the results of previous investigators (references cited earlier). Vitrains with carbon contents of 74.5% and higher, plotted on the diagram, are Australian materials from all States except the Northern Territory; their geological ages range from Permian to Jurassic, and the metamorphic conditions under which they have been coalified vary considerably. The moisture-rank zone for these materials becomes very narrow and reaches a minimum at about 88% carbon, which agrees with the relationship previously established for coals from other countries.

On the low-rank side (55% to 75% carbon) of the diagram in Fig. 1, there is evidence of a prominent maximum at about 67% carbon. This maximum does not appear to have been recorded by previous investigators, and it is believed that it is an important characteristic of the moisture-rank relationship. It occurs at immature brown-coal rank, and probably corresponds to the maximum degree of colloidal development attained during coalification, suggesting that the substance of wood undergoes a slow process of physical disorganization during the peat stage to become a watery gel at about immature brown-coal stage, where

inherent moisture reaches its maximum. Decrease of inherent moisture on the high-rank side of the maximum would seem to be associated with the closing up, or maturing, of the micelle structure in the gel as physical rank is advanced by pressure from overlying beds and moderate earth temperatures operating over long periods of time.

The results indicating a maximum in the moisture-rank zone, on the low-rank side of Fig. 1, were obtained for woody materials occurring in brown coals in England, Germany, Canada and Australia, and ranging in geological age from Cretaceous to Pleistocene. This, together with the continuity of the zone throughout all ranks, and the agreement between zones for Australian vitrains above 74% carbon and for coals of similar rank from other countries, indicates that the same general moisture-rank relationship applies to all coals irrespective of their position in the world, the botanical species of original organic debris from which they were formed, or the exact conditions of metamorphism under which they were coalified.

The zonal nature of the moisture-rank relationship appears to be a consequence of independent advancement of physical and chemical ranks (Dulhunty, 1947a). In constructing the moisture-carbon graph, a factor associated with physical rank is plotted against one depending on chemical rank. The two ranks advance at the same time, but either may become more advanced than the other depending on conditions of metamorphism. This gives rise to a certain variation in moisture values for coals of any given carbon content, resulting in a zonal relationship. It follows that the varying width of the zone may be regarded as an expression of the extent to which chemical and physical ranks may differ in advancement during coalification.

RELATIONS OF RANK TO PERMANENT REDUCTION OF MOISTURE ON DRYING.

Results of previous work have shown that low-rank coals undergo permanent changes in hardness, lustre and inherent moisture when dried from their original water-saturated condition (Dulhunty, 1946 and 1948). The present investigation was undertaken with the object of determining the range in rank over which permanent reduction in moisture takes place when vitrain is dried, and also the relationship between the extent of reduction and rank.

Vitrains used were those, listed in Table 1 and included in Fig. 1, which had been collected and maintained in their original water-saturated condition. Maximum inherent moisture in the original water-saturated condition had already been determined in connection with work described earlier. Additional portions of the same vitrain samples were oven-dried at 105° C. in a stream of dry nitrogen until their weights were constant. They were then evacuated for one hour at room temperature using a vacuum pump capable of reducing pressure to 0.0003 mm. of mercury. The evacuation was carried out in a tube connected by means of a carefully ground glass cock to a vessel containing air-free water and water vapour. After pumping down for one hour, the vacuum line was shut off and the cock connecting with the air-free water was opened, allowing water vapour and liquid water to enter the tube containing the evacuated vitrain. When the vitrain was thoroughly wet and covered with water, the tube was opened and air allowed to enter. The vitrain was then allowed to stand under water for 24 hours, before draining and filling into the conditioning tubes of the apparatus for determination of maximum inherent moisture by controlled vaporization of adherent moisture.

Results for maximum inherent moistures determined on the vitrains in their original water-saturated condition, and after having been oven-dried and resaturated, are summarized in Table 2. It is evident that all materials with

carbon contents of 76.6% and lower underwent marked reduction of inherent moisture as a result of drying. Those with carbon contents higher than 76.6% do not appear to have suffered any such change, as the two moisture values for each vitrain are within the limits of reproducibility for the method of determination (Dulhunty, 1947). Therefore it was concluded that vitrains containing more than about 78% carbon do not undergo permanent reduction of inherent moisture when oven-dried.

It has been suggested that all coals suffer a certain amount of permanent reduction in inherent moisture when oven-dried. As a result of the foregoing work it is believed that vitrains containing more than 78% carbon, and probably all coals of similar rank, can be oven-dried and resaturated to their original

TABLE II.

Relations between Rank and Permanent Reduction of Moisture on Drying.

(For further data, see Table I.)

Spec. No.	Carbon %. (A.F.D.)	Max. Inher. Moist. % (A.F.D. Basis).	
		Original Water- Saturated Condition.	Oven-dried and Re- saturated.
312-314	88.6	1.88	1.90
460	84.1	5.77	5.74
458	83.7	4.01	3.92
459	83.4	4.81	4.68
288	82.0	13.35	13.36
461	79.8	6.10	6.10
317	76.6	26.20	22.55
304	74.5	67.50	33.70
457	70.5	61.45	20.95
456	69.8	85.00	31.40
88	68.9	78.82	29.95
454	68.3	94.60	49.50
136	67.4	118.30	37.70
455	62.5	69.30	43.20
104	59.2	61.3	32.55
453	58.2	38.75	36.90

maximum inherent moistures if the drying is carried out in an atmosphere of nitrogen; if resaturation is sufficiently complete, and if the moisture values represent true inherent moisture and not varying amounts of adherent moisture.

In previous publications (Dulhunty, 1946, 1948) it was suggested that low-rank coals undergo permanent reduction of inherent moisture on drying as a result of deformation of the micelles, and reduction of intervening spaces, under the influence of attractive forces between the micelles when internal pressure of adsorbed water is released by drying. From the present results it would appear that medium to high-rank vitrain, containing more than about 78% carbon, has reached a degree of maturity at which the micelle structure is sufficiently rigid to withstand the forces of inter-micelle attraction without deformation when adsorbed water is removed.

The relationship between rank and extent of permanent reduction of inherent moisture on drying is illustrated in Fig. 2. This diagram was constructed by

plotting moisture values against carbon for each of the materials in Table 2. In the case of vitrains which showed permanent reduction, values for maximum inherent moisture in the original water-saturated condition and after oven-drying and resaturating are joined by vertical lines which indicate the extent of permanent reduction. Vitrains which did not undergo permanent reduction are shown as single points on the diagram. Curves were drawn through the two sets of points for vitrains showing permanent reduction. These curves form a zone the width of which represents approximately the amount of permanent reduction suffered by vitrains of different rank up to about 87% carbon. At this rank the two curves meet, and a single line drawn through the vitrains of higher rank indicates no permanent reduction of moisture on drying.

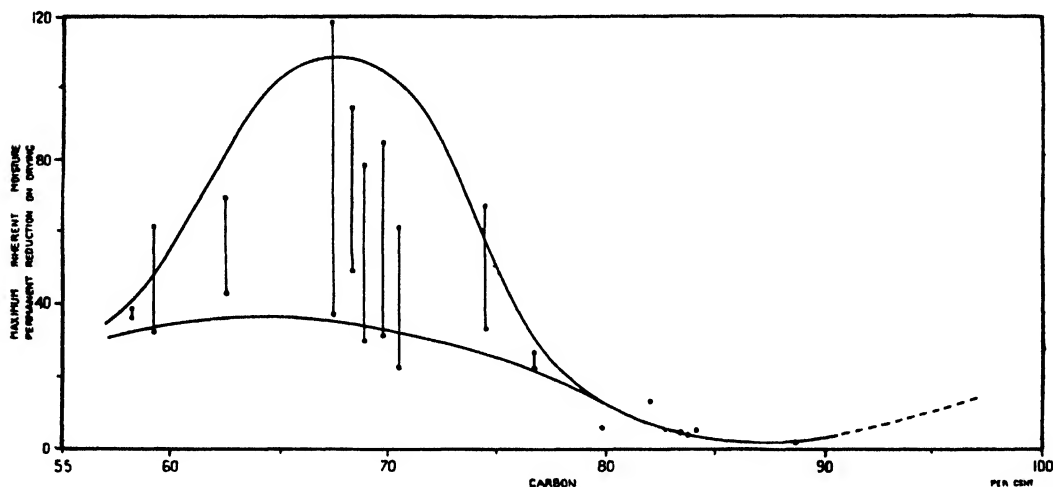


Fig. 2.—Diagram illustrating relationship between rank and extent of permanent reduction of moisture on drying vitrain, and range of rank over which permanent reduction takes place.

The complete diagram (Fig. 2) illustrates the range of rank (approximately 55% to 78% carbon) over which vitrain undergoes permanent reduction of inherent moisture on drying, and also shows that the amount of reduction for low-rank vitrain is related to rank. It is evident that the amount of reduction is greatest at the rank-stage where inherent moisture reaches its maximum in the moisture-rank relationship (Fig. 1). This supports the conception, discussed earlier, that vitrain attains its maximum degree of colloidal development at the rank where maximum inherent moisture is greatest. The watery gel formed at that rank, with soft immature micelle, would provide the optimum conditions for deformation of micelles, closing up of inter-micelle spaces, and the formation of larger inter-micelle contact areas, as a result of attractive forces operating when adsorbed water is removed by drying.

SUMMARY OF RESULTS.

As a result of investigations outlined in this paper, it is concluded that :

(1) The relationship between maximum inherent moisture and rank of vitrain is characterized by a minimum in moisture at about 88% carbon (as previously established for coal samples), and a maximum in moisture at about 68% carbon (not previously recognized).

(2) Vitrains with carbon contents varying from about 55% to 75% undergo permanent reduction in maximum inherent moisture when oven-dried. Those of higher rank are not effected in this way.

(3) The extent of permanent reduction in inherent moisture increases with rank to about 67% carbon where it reaches a maximum. It then decreases to zero at about 78% carbon.

(4) The maxima reached by inherent moisture and permanent reduction of moisture on drying (at about 57% carbon) are both a consequence of a maximum in the degree of colloidal development attained by vitrain at the same rank.

ACKNOWLEDGEMENTS.

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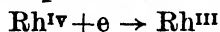
THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART XI. THE POTENTIAL OF THE TRIVALENT-QUADRIVALENT RHODIUM COUPLE IN SULPHURIC ACID.

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and H. N. SCHAFER, B.Sc.

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Grube and co-workers (1937) studied the electrolytic oxidation of rhodium III salt solutions and measured the potential of the system



The potential was found to vary from 1.363 volts in 0.154 N sulphuric acid to 1.434 volts in 1.00 N acid, and was notably unsteady in all acid concentrations, so that the final value quoted was 1.4 volts. In the present investigation the aim was to measure the potential more accurately and in solutions of greater acid concentration so as to obtain some insight into the form of the higher valent state.

Cells of the following types were measured.



The potential of the saturated calomel electrode was checked against a quinhydrone electrode in potassium hydrogen phthalate at pH 4, and the value 0.2443 volt at 25° C. accepted. The cell assembly was similar to that used in previous determinations (Dwyer, Nyholm and McKenzie, 1944).

Since the system was found to be very slow in reaching equilibrium, as noted by Grube (*loc. cit.*), cerous sulphate was added as a potential mediator. This mediator was chosen since the redox potential of the cerous-ceric couple in sulphuric acid (1.45 volts) is close to the system being measured. One drop only of 0.0875 M solution in 0.2 N sulphuric acid was found to cause the potential to rise rapidly. Addition of further cerous salt did not affect the potential, but large amounts (1–2 c.c.) caused the potential to fall. In the presence of the mediator a steady potential was reached in 24 hours, and was not affected by stirring the solution. Curiously enough, the system was light-sensitive, the illumination from a 50-watt lamp at a distance of two feet causing the potential to fall by four or five millivolts. In the dark the potential rose immediately to the original value. All the measurements have been carried out in the darkness or in diffuse light.

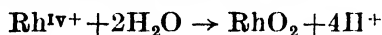
The system was also found to be badly "poised", and the potentials were therefore determined with a valve potentiometer. With the Leeds and Northrup Type K potentiometer the potential fell very rapidly, whilst measurements were being made, finally coming to equilibrium 150 to 200 millivolts below the initial reading. If the lead from the platinum electrode was disconnected, however, the potential rose again slowly—more rapidly if the solution was vigorously stirred—and the initial high potential was reached in about 30 minutes.

The rhodium III sulphate in sulphuric acid of the appropriate concentration was oxidized, so that approximately half of the rhodium was in the quadrivalent state, in order that the correction for lack of equimolarity of the oxidized and reduced forms would be as small as possible. The potential on the bright

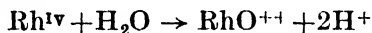
platinum electrode in the presence of the mediator was determined, and when equilibrium had been reached the solution was immediately titrated potentiometrically with ferrous sulphate solution. Experiments showed that the loss of rhodium by diffusion during the anodic oxidation to rhodium IV was very small, and hence the amount of rhodium III was taken as the total rhodium less the oxidized rhodium. The activities of the oxidant and reductant ions are not known, hence concentrations have been used in the calculations.

$$\text{Then } E = E_0 + 0.05915 \log \frac{[\text{Rh}^{\text{IV}}]}{[\text{Rh}^{\text{III}}]} \text{ at } 25^\circ \text{C.}$$

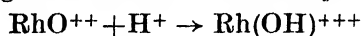
The potential of the system was found to rise very sharply up to an acid concentration of 1 normal, and then in the range from 1 N to 6 N varied only from 1.43 v. to 1.440 v. In the lower acid concentrations the oxidized solutions appeared to be turbid and the low potentials are thus probably due to extensive hydrolysis and the separation of rhodium dioxide.



The almost complete independence of the potential and the acid concentration at higher acidities is difficult to explain. As suggested by Latimer (1940), rhodium IV is unlikely to exist in solution as a tetrapositive ion, but could exist as the oxy ion RhO^{++} :



Complex ion formation which should occur in the higher acidities and chiefly with the oxidant ion would lower the potential. It is evident that complex ion formation does not occur and the very slight rise in the potential must be due either to more complete reversal of the hydrolysis as shown in the first equation or alternatively to a change in the form of the oxy ion RhO^{++} to $\text{Rh}(\text{OH})^{+++}$:



There is evidence that the ion in iridium IV solutions, at present being studied, may exist in at least two forms, whilst Grube (*loc. cit.*) has noted that the colour of rhodium IV solutions may vary, and has ascribed the effect to hydrate isomerism.

EXPERIMENTAL.

Preparation of Solutions.

Rhodium III Sulphate. Approximately 1 g. of rhodium sponge was dissolved by fusion in potassium bisulphate, and the resulting bright yellow mass extracted with water and filtered from traces of undissolved metal. The hydroxide was precipitated from boiling solution with sodium carbonate, and after thorough washing dissolved in sulphuric acid. The rhodium was estimated by reduction with hydrazine in alkaline solution, and ignition in a reducing atmosphere, and subsequently the solution was adjusted to be M/100 with respect to rhodium and N/2 with respect to sulphuric acid.

Rhodium IV Sulphate. The rhodium III sulphate solution, 20–25 cc., was placed in a small sintered glass Gooch crucible, dipping into N/2 sulphuric acid in a small beaker, and the levels inside and out rapidly adjusted so that no flow of liquid took place through the membrane. With a stout platinum wire spiral anode, and a lead cathode, the oxidation was carried out until 40–60% oxidation had occurred. The solution in the anode compartment at this stage had become greyish green in colour.

Measurement of the Potential. The oxidized rhodium solution, 20 cc., was placed in the redox cell, followed by sufficient sulphuric acid to give the required acid concentration, and the volume then made up to 30 cc. with distilled water. The cell solutions were thus approximately M/300 with respect to the oxidant and reductant ions. After the addition of the cerous sulphate mediator the solution was stirred continuously until equilibrium was reached. The concentration of the oxidant ion was then immediately determined in the redox cell by titration with N/100 ferrous sulphate solution.

The values of the potential E and the corrected E_0 values are shown in Table I.

TABLE I.

Acid Conc.	Rh ³ gms.	Rh ⁴ gms.	E (obs.).	Correction.	E_0
0.5 N	0.0108	0.0098	1.377 ₅	0.0025	1.380
0.7	0.0126	0.0080	1.412 ₅	0.0115	1.424
1.0	0.0116	0.0090	1.428 ₅	0.0067	1.435
2.0	0.0111	0.0095	1.433 ₆	0.0041	1.437
3.0	0.0106	0.0100	1.437 ₄	0.0016	1.438
4.0	0.0115	0.0091	1.423 ₅	0.0062	1.439
5.0	0.0108	0.0098	1.437 ₅	0.0025	1.440
6.0	0.01111	0.0095	1.436 ₅	0.0041	1.440 ₄

SUMMARY.

The potential of the trivalent/quadrivalent rhodium couple in sulphuric acid solution has been found to vary from 1.380 volts in 0.5 N acid to 1.440 volts in 6 N acid. There was no evidence of complex ion formation in the concentrated acid solutions, and the oxidant ion appears to be RhO^{++} .

ACKNOWLEDGEMENT.

The authors are indebted to the Commonwealth Research Fund for a grant for the purchase of rhodium.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART VII. GEOLOGY OF THE BOGGABRI DISTRICT.

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With Plate XIX.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The area covered by this paper adjoins the Gunnedah-Curlewis district (Hanlon, 1948*a*) on the south and the south-western part of the County of Nandewar (Hanlon, 1948*c*) along the Namoi River to the east. It extends northwards to the old surveyed town of Turrawan on the Namoi River and includes all known outcrops of Permian strata within the North-western Coalfield, north of Gunnedah and west of the Namoi River.

The survey was in the nature of a reconnaissance. A telescopic alidade traverse was made from Boggabri Railway Station to the Triassic beds outcropping to the west of the town, in order to give accurate figures on which to base estimates of the thickness of the Permian strata.

TOPOGRAPHY AND ACCESS.

Boggabri is the most important town in the district. It is situated on the North-western Railway line, being 320 miles from Sydney and 823 feet above sea level.

Access by road is good and main roads connecting with Gunnedah, Narrabri and Manilla are trafficable in practically all weathers. However, many of the secondary roads which cross the black soil plains become impassable after any appreciable rains.

Physiographically, the Boggabri district can be divided into three main types. These are the extensive alluvial flats along the Namoi River and its tributaries, Cox's Creek to the south of Boggabri and Tulla Mullen Creek to the north; the gently undulating areas where the Triassic and Permian strata outcrop; and the group of hills which rise steeply about 300 to 400 feet above the general surrounding level and are composed of Lower Marine lavas. Mount Binalong is an exceptional feature. It is composed of Tertiary dolerite and basalt. The summit is the highest point in the district and is approximately 1,700 feet above sea level.

GEOLOGY.

The geological formations comprise the following, which will be described in order, commencing with the oldest.

Tertiary to Recent alluvium.

Tertiary Igneous Rocks.

Triassic.

Permian—

Upper Coal Measures—Booroomin Group.

Lower Marine Series—Boggabri Volcanics.

Permian.

Only portion of the Permian sequence is present in the Boggabri district. The Lower Marine Series is represented solely by lava flows and the Upper Coal Measures is the only group of sedimentary beds which is definitely present. The Upper Marine Series may be represented, although there is no fossil evidence to support the suggestion. The Lower Coal Measures do not appear to outcrop.

Lower Marine Series. The Lower Marine lava flows which outcrop in the vicinity of Boggabri have been named the Boggabri Volcanics (Hanlon, 1948c). West of the Namoi River they consist mainly of rhyolites and felsites. At a few points, as for example at the foot of Robertson's Mount, rhyolites pass laterally into pitchstones. Near The Rock, in portion 145, Parish of Bogabri, County of Pottinger, the pitchstone appears to be in the form of a dyke intruding a more basic flow, which is much weathered at the present time. The dyke must have been intruded in a very fluid condition and reached close to the surface in order to account for the rapid cooling necessary to form the pitchstone. It is also unlikely, for the same reason, that any large amount of magma flowed through the channel.

Amygaloidal basalts occur in places, but are subordinate to the more acid types, at least as far as can be judged from outcrops. There appears to be a consistent diminution in the proportion of basalts in the Lower Marine sequence, as the beds are traced in a north-westerly direction. In the Werrie Basin (Carey, 1934, 1935) the Werrie Basalts preponderate, at Gunnedah the basalts and acid lavas are both well represented, while near Boggabri the acid lavas form the great bulk of the outcrops.

Upper Coal Measures. It is proposed to name the Permian sedimentary rocks the Booroomin Group, because the best section of them is obtained on a property of that name, to the west of Boggabri. The upper part of the sequence is exposed on hillslopes and the lower beds outcrop between there and the township of Boggabri. Some details of the lower beds can also be obtained from a bore sunk on "Booroomin", in portion 175, Parish of Bogabri. At other points in the district only the upper beds are exposed.

It is difficult to give an accurate estimate of the thickness of the Booroomin Group. The difference in height between the basal beds near Boggabri Railway Station and the base of the Triassic west of the town is 400 feet. The dip of the uppermost beds is generally in a west-south-westerly direction at between 1 in 100 and 1 in 30. If it be assumed that the dip is constant between "Booroomin" and Boggabri, the figures quoted would give a thickness for the Booroomin Group ranging between 550 and 900 feet. The bore referred to above is located 250 feet below the base of the Triassic and passed through 520 feet of sediments, allegedly striking 8 feet of coal at a depth of 502 feet. This would give a total thickness for the Booroomin Group in excess of 770 feet. Whatever the maximum thickness may be, the thickness at different places varies considerably, the sediments having been laid down on the eroded surface of the Lower Marine lavas.

The Booroomin Group is composed of sandstones, conglomerates, shales, thin limestone bands and coal seams, but the sequence differs materially from that of the type section of the Upper Coal Measures at Gunnedah. The topmost beds comprise sandstones and conglomerates, 60 to 70 feet thick. The pebbles in the conglomerates consist mainly of acid lavas, but some of the pebbly bands in the sandstones contain appreciable quantities of white quartz pebbles. This zone is underlain by shales containing *Glossopteris* and the weathered spoil of coal occurs on two horizons about 15 feet apart. Beneath the coal there are about 60 to 70 feet of shales and sandstones. The underlying beds form poor outcrops and as far as can be judged, comprise shales with bands of sandstone

GEOLOGICAL MAP

BOGGABRI DISTRICT

COUNTY OF POTTINGER

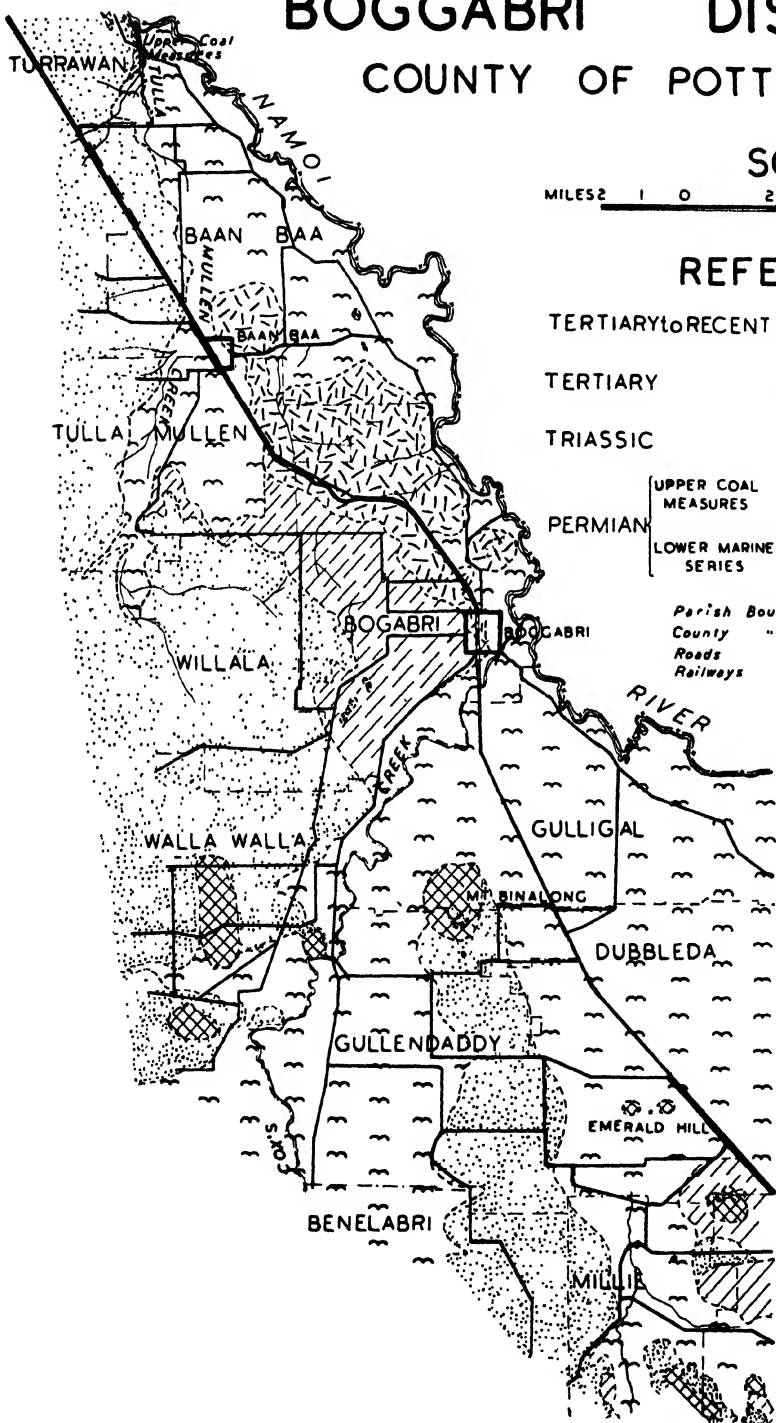
SCALE

MILES 2 1 0 2 4 6 8 MILE

REFERENCE

TERTIARY to RECENT		Alluvium
TERTIARY		Dolerite
TRIASSIC		Sandstones and basal conglomerates.
UPPER COAL MEASURES		Booroomin Group: Sandstone, shales, conglomerates, band of limestone and coal seam
PERMIAN LOWER MARINE SERIES		Boggabri Volcanics: Rhyolites, felsites and pitchstones

Parish Boundaries
County "
Roads "
Railways "



and impure limestone. The latter are concretionary, at least in part. These beds are in turn underlain by sandstones and conglomerates, which rest directly on the eroded surface of the Lower Marine lavas near the town of Boggabri. The pebbles in the basal beds are composed of acid lavas similar to the underlying Lower Marine flows. The bore in portion 175, as far as can be judged from the log provided, passed through sandstones and shales to a depth of 422 feet, then through 69 feet of conglomerates, 11 feet of sandstone, 8 feet of coal and 10 feet of shales. However, as it was a percussion bore and the drillings were not examined by a geologist, too much reliance could not be placed on the log supplied.

The position of the upper coal horizon in fossiliferous shales, underlying sandstones and conglomerates containing bands of white quartz pebbles, suggests that it may be developed on or close to the horizon of Hoskisson's Seam, although it is only 100 feet below the base of the Triassic instead of about 240 to 300 feet below as in the type area at Gunnedah (Hanlon, 1948a). This would mean that, as at Breeza (Hanlon, 1948b), the upper portion of the sequence in the type area, that is, above the sandstone with the white quartz pebbles, is missing in the Boggabri district.

The increased thickness of the beds when compared with the sequence in the Gunnedah area, especially if the upper portion of the sequence be missing, would suggest that some of the lower beds may be of Upper Marine age. The zone of shales with sandstone and impure limestone bands, overlying a zone of conglomerates and sandstones, is also suggestive of the Upper Marine sequence at Gunnedah. The coal in the bore in portion 175, 750 feet below the base of the Triassic and 650 feet below the upper seam, does not correspond to coal developed anywhere in the Gunnedah area, unless a thickening of the intervening beds is postulated. This also raises the suggestion that this coal could form part of the Lower Coal Measures, developed below Upper Marine beds. However, a careful search of the beds failed to reveal any marine fossils, and in these circumstances it is considered advisable to classify all the beds as Upper Coal Measures.

Several bores sunk for water between Gunnedah and Boggabri have struck coal. The alluvium and perhaps some of the lower parts of the hillslopes, east of the Triassic beds in this area, are probably largely underlain by the Upper Coal Measures. North-west of Boggabri the coal measures can be traced as far as Tulla Mullen Creek, in portion 77, Parish of Tulla Mullen. The only outcrop north of this point is a restricted occurrence about ten miles downstream along Tulla Mullen Creek, near its junction with the Namoi River in the Parish of Turrawan, County of White. The beds underlie Triassic conglomerate, but the only fossil evidence found was very abundant silicified wood. Coal is alleged to have been struck in a bore on the creek flat near by, at a depth of about 80 feet.

Triassic.

The Triassic beds comprise the basal conglomerates with abundant jasper pebbles, which are so characteristically developed throughout the North-western Coalfield, and sandstones. Ferruginous altered rocks, which occur in portion 18, Parish of Gorman, County of White, have been identified as tuffs (?).

The basal conglomerates overlying the Upper Coal Measures sandstones, west of Boggabri township, form a massive bed, but are only about 20 feet thick. South of Mount Binalong the beds appear to weather easily and outcrops are represented by loose pebbles. At some localities, conglomerates seem to be developed on more than one horizon in the lower part of the Triassic sequence, and in portion 118, Parish of Gullendaddy, there appear to be three horizons of conglomerates separated by sandstones.

The overlying sandstones are thinly bedded and to the west and south of Boggabri form low escarpments in several places. However, over much of the area the sandstones form poor outcrops and much of the area underlain by these

beds is covered with loose sand rising above the adjacent alluvial flats. This type of weathering to sandy wastes is very characteristic of Jurassic sandstones in many places. It raises the possibility that some of these beds may be of Jurassic age, although they could easily be Triassic sandstones which have weathered more completely owing to their having a different or inferior cementing agent in this section of the North-western Coalfield.

There is no fossil evidence on which to base an estimate of the age of any of the Mesozoic strata. The basal Triassic conglomerates do not outcrop between portion 77, Parish of Tulla Mullen, County of Pottinger, and portion 41, Parish of Turrawan, County of White, in which places they can be seen overlying Upper Coal Measures. It may be that the sandy wastes north of Baan Baa represent Jurassic sandstones which have overlapped the Triassic beds in the area. Near Baan Baa itself, although the Upper Coal Measures may occur beneath the alluvium, it is almost certain that they were overlapped in Mesozoic times, because Mesozoic beds are found within less than 50 chains of Lower Marine lavas that rise considerably above the level at which the sediments occur.

Tertiary Igneous Rocks.

The alkaline suite of Tertiary rocks, comprising rhyolites, trachytes, trachyandesites and andesites, which are found associated with the Boggabri Volcanics east of the Namoi River, appear to be absent, or if present, must form only a minor proportion of the outcrops.

The Tertiary igneous rocks mapped consist entirely of dolerites and basalts, and in most instances were intruded in the form of sills. The greatest thickness is at Mount Binalong, where the northern slope appears to be composed entirely of igneous material and would represent a total thickness of at least 900 feet. Specimens collected from the top of the mountain were monchiquitic in composition. Both olivine and analcite are abundant in the dolerites. Some of the amygdaloidal basalts associated with the Boggabri Volcanics may also be of Tertiary age.

Tertiary to Recent.

The only sedimentary deposits of these ages are the deposits of alluvium along the Namoi River and its tributaries. The largest expanse is along the Namoi River east of Mount Binalong and along Cox's Creek to the west. Around Boggabri, where the Namoi flows through the area occupied by the Lower Marine lavas, the alluvium is much restricted. Further north it widens again and there are considerable areas along Tulla Mullen Creek and along the Namoi River itself. The alluvium is of the "black soil" variety, similar to that described for other parts of the North-western Coalfield.

STRUCTURAL GEOLOGY.

The structure of the area represents the northerly continuation of the relatively simple structures of the Gunnedah area. Both folding and faulting are of a minor nature.

The area in which the Lower Marine lavas outcrop probably represented an old structural high to the east of which sedimentation took place in Lower Coal Measures time. West of this high the Lower Coal Measures were developed to a much lesser extent, if at all, and the Upper Coal Measures (and possibly Upper Marine Series) was laid down on the eroded surface of the Lower Marine lavas. The Triassic beds appear to overlie the Upper Coal Measures conformably. The Triassic (or possibly Jurassic) would appear to have overlapped the coal measures near Baan Baa and to have rested directly on the Lower Marine lavas. Whether the Triassic beds may have been overlapped in turn at some points it is impossible to say.

ACKNOWLEDGEMENTS.

I was assisted by Mr. J. C. Lloyd, B.Sc., and many helpful discussions with him during the course of the work are gratefully acknowledged. I am indebted to Mr. H. F. Whitworth, M.Sc., Curator of the Mining Museum, for the petrological determinations. I also wish to express my thanks to Mr. J. E. Lancaster, Under Secretary for Mines, and Mr. C. St. J. Mulholland, B.Sc., Government Geologist, for permission to publish this paper.

SUMMARY.

The Permian sediments comprise only the Upper Coal Measures, which have been deposited on the eroded surface of the Boggabri Volcanics (Lower Marine). The coal measures are overlain conformably by Triassic beds and Jurassic sandstones may possibly occur. The sediments have been intruded by Tertiary dolerite sills and there are also extensive alluvial areas. The structural geology is simple.

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GEOLOGY OF THE NORTH-WESTERN COALFIELD, N.S.W.

PART VIII. GEOLOGY OF THE NARRABRI DISTRICT.

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With Plate XX.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The Narrabri district comprises most of the northern half of the County of Nandewar, north of Maules Creek, together with small sections of the Counties of Jamison, Murchison, Pottinger and White. It adjoins the South-Western part of the County of Nandewar (Hanlon, 1948*a*) along Maules Creek, and the Boggabri District (Hanlon, 1948*b*), near the old surveyed town of Turrawan.

The geology of the area was described previously by Jensen (1907), who was mainly interested in the petrology of the Tertiary igneous rocks. Some of the boundaries between the sediments and the Tertiary igneous rocks have been adapted from his map. However, the classification of the Permian strata and their disposition and relationships with the Triassic and Carboniferous beds, as set out in this paper, are the author's work. The Narrabri district also overlaps, at one point, the area mapped by Benson (1917), east of the Nandewar Mountains.

The survey was in the nature of a reconnaissance. The rough terrain and the extensive Tertiary intrusions and lava flows, with resultant heavy talus cover on steep slopes, rendered accurate mapping of boundaries difficult and in some places impossible. The boundaries of the Permian with the Triassic and Carboniferous beds are accurate within the limits of the survey methods used except in areas where they have been intruded or covered by Tertiary igneous rocks.

TOPOGRAPHY AND ACCESS.

The only town in the district is Narrabri. (West Narrabri is adjacent to it and is located on the opposite or western side of the Namoi River.) The main part of the town is situated along Narrabri Creek, a tributary of the Namoi River. The North-western Railway line passes through the town and connects with Moree to the north and Boggabri to the south. Branch lines connect with Walgett and Pokataroo. Narrabri is 353 miles from Sydney and is 697 feet above sea level.

Access by road varies considerably. Over the flatter sections access is good, except that many of the roads become impassable after any appreciable rains. On the other hand there are very few roads in the mountainous section of the area and many points are accessible only on foot.

Topographical relief is considerable and the area can be divided into three main zones, a low-lying section, an intermediate zone, and the Nandewar Mountains proper. The low-lying section is mainly covered by alluvium and is situated along the Namoi River and the lower part of Maules Creek. Outcrops which rise above the general plain level reach only a moderate elevation. The



intermediate zone is composed largely of Permian and Triassic beds, which have been intruded and in places covered by Tertiary igneous rocks. The surface slopes generally to the south-west, away from the main mass of the Nandewar Mountains. The creeks, which in the plains form only insignificant watercourses, tend to occupy narrow gorges, and ground suitable for cultivation is confined to a narrow strip along the floor of the gully. The Nandewar Mountains proper are composed mainly of igneous rocks and relief is considerable. The highest point is Mt. Kaputar, 5,000 feet a.s.l., and many peaks along the main line of the range rise well above the 4,000 feet level. A branch spur extends west-south-westerly from the vicinity of Mt. Kaputar, and on it the peaks Coryah, Yulludunida and Ningadhun are located.

GEOLOGY.

The geological formations comprise the following, which will be described in order, commencing with the oldest.

Tertiary to Recent alluvium.

Tertiary Igneous rocks.

Triassic.

Permian—

Upper Marine Series—Barra Group.

Lower Coal Measures—Nandewar Group.

Carboniferous—

Upper Kuttung Series—Rocky Creek Conglomerates.

Carboniferous.

The Carboniferous beds form the northerly continuation of the Upper Kuttung beds mapped previously to the south of Maules Creek (Hanlon, 1948*a*). They are the equivalents of the Rocky Creek Conglomerates described by Benson (1917), and comprise conglomerates, which are often coarse, interbedded with tuffs and acid lavas. The rocks have not been studied in detail and only their western boundary has been mapped.

Permian.

The coal-bearing strata in the Narrabri District have always been regarded as belonging to the Upper Coal Measures. It now appears that they form part of the Lower Coal Measures and that the Upper Coal Measures are missing, being overlapped by the Triassic, which rests directly on Upper Marine beds. In the northern and eastern sections of the district, the Upper Marine seems to be overlapped in turn and it is likely, at least to the north, that the Triassic beds rest directly on the Lower Coal Measures. Lower Marine beds do not outcrop in the area and it is unlikely that the lavas of this age, found further south, are developed. However, if they were developed, the lack of outcrops could easily be explained as being due to their elimination by the faulting which occurs in the area.

Lower Coal Measures. The Greta age of these beds has been established by the discovery of Upper Marine fossils in the overlying beds. They represent the northerly continuation of the Nandewar Group, (Hanlon, 1948*a*), which has been mapped to the south of Maules Creek. They comprise conglomerates, sandstones and shales with coal seams. Plant remains are very abundant on several horizons in the shales. Many of the fossiliferous bands are heavily iron-stained and contain ironstone concretions. Fossil wood is also very abundant, at times the wood being entirely replaced by ironstone. The best collection of fossil leaves was obtained from portion 47, Parish of Billyena, County of

Nandewar, on the southern slopes of Black Mountain. The following forms have been identified :

**Noeggerathiopsis hislopi* Feistmantel.

Glossopteris browniana Brong.

Glossopteris tortuosa Zeiller.

Glossopteris indica Schimper.

Glossopteris cf. *jonesi* Walkom.

The thickness of the Permian strata in the neighbourhood of the boundary between the Parishes of Billyena and Deriah must be at least of the order of 1,000 feet. Whether the upper section of these beds is of Upper Marine age it is not possible to say in the absence of any fossil evidence, and all the beds have been mapped as Lower Coal Measures. It is also not possible to say whether the whole of the Nandewar Group developed further south is represented in the area. The Wean Formation is certainly present, but the Vickery Conglomerates does not occur as such. The upper section of the sequence in portions 3 and 114, Parish of Billyena, is composed mainly of sandstones with conglomerate bands. No fossils were found in it and it could represent the Vickery Conglomerate. The change in facies would not need to be sudden, because the type area in which the Vickery Conglomerate is developed is 20 miles away. A careful search for fossils in the area may yield valuable information as to the easterly limits of the Upper Marine beds and also enable the age of the Vickery Conglomerate to be determined more definitely.

The most widespread outcrops of the Nandewar Group are in the Black Mountain Creek area. They are also well represented in the upper reaches of Bullawa and Bobbiwaa Creeks and their tributaries, and probably occur along the bed of portion of Eulah Creek, although no recognizable outcrops were seen. In areas which have been intruded by Tertiary igneous rocks, some blocks have been carried well above the positions they would occupy normally, and now occur above the level of adjacent Triassic beds. This applies particularly to the Killarney Gap area, coal measures outcropping along the divide where the main road between Narrabri and Bingera crosses the range, while *Thinnfeldia* has been found in shaley bands in sandstones at the foot of the mountains.

The only information available as to the thicknesses of the coal seams is that provided by wells and percussion bores. The outcrops of any seams examined were perished. In the absence of analyses or the availability of fresh samples for examination, it is not possible to form a definite opinion as to the quality of the coal. The general impression gained is that the seams would be of fair quality, but may only be thin.

Upper Marine Series. It is proposed to refer to the Upper Marine beds as the Barra Group, the maximum development of definite marine beds being north of Barra Creek, in portion 80, Parish of Eulah, County of Nandewar. It is impossible to obtain good sections of the beds or give any reliable figures for their thickness, because of the talus cover on steep slopes. In the type locality the beds are found over a range in height of several hundreds of feet. However, in an adjacent tributary creek they appear to be absent, the only outcrops below the Triassic being Tertiary dolerite. Further east in portion 78, Parish of Eulah, the beds are only a few feet thick, being overlain by Triassic conglomerate and underlain by Tertiary dolerite. The dolerite may extend westwards in the form of a sill or sills in the Upper Marine beds and account for a large proportion of the thickness over which they occur. It is probable that the maximum thickness is of the order of 200 feet.

* There is a considerable variety in size in *N. hislopi* and more than one species may be represented.

The possibility that some of the beds mapped as coal measures further east may belong to the Upper Marine has been discussed above. If these beds should be Upper Marine, the maximum thickness would exceed the 200 feet quoted.

The most comprehensive suite of fossils was obtained from portion 80, Parish of Eulah, and comprised the following forms:

Protoretepora ampla Lonsdale.

Fenestrellina spp.

Spirifer duodecimcostata McCoy.

Terrakea brachythæra Sowerby.

Mæonia carinata (Morris).

Stutchburia compressa (Morris).

Edmondia nobilissima de Koninck.

Dun (1909) identified *Protoretepora*, *Spirifera*, *Mæonia carinata*, *Pachydomus* and *Ptychomphalina* in a collection of fossils by Mr. L. F. Harper, who probably obtained them from the same locality.

In portion 78, Parish of Eulah, the following forms were found in a band of impure limestone overlying a dolerite sill and within a few feet of the basal Triassic conglomerate.

Terrakea brachythæra (Sowerby).

Ptychomphalina morrisiana McCoy.

Conglomerates and sandstones occur in portion 11, Parish of Deriah, overlying coal measures, and in turn overlain by Tertiary dolerite. The following forms were collected from these beds.

Terrakea fragile (Dana).

Fenestrellina sp.

Spirifer duodecimcostata McCoy.

This occurrence is of particular interest because it proves the underlying fresh water beds belong to the Lower or Greta Coal Measures.

Triassic.

The Triassic rocks consist mainly of sandstones with basal conglomerates. Thin shaley beds occur, but form only a very minor proportion of the full sequence. The only fossil evidence as to their age was one poorly preserved specimen of *Thinnfeldia* sp. obtained from an outcrop on the side of the Killarney Gap road in portion 17, Parish of Cowimangarah, County of Jamison.

The basal conglomerates are similar to those developed in other parts of the North-western Coalfield, being characterized by the occurrence of jasper pebbles. However, in parts of the area the jasper pebbles do not preponderate to the same extent as further south. In the vicinity of Bibbla, Deriah, Bullawa and Eulah Creeks pebbles of acid lavas are abundant and the jasper pebbles are sometimes subordinate.

The overlying sandstones are several hundreds of feet thick and in places are very thinly bedded. This seems to be particularly the case with beds in the lower part of the sequence, close to the basal conglomerates. Higher in the sequence the beds are more massive. The Triassic sandstones are probably overlain by Jurassic sandstones and may be partly overlapped by them. The basal conglomerates, too, may be overlapped in places. North, south and west of Narrabri, Jurassic strata must have been deposited and would have connected with the Jurassic beds which outcrop between Narrabri and Warialda in one direction and Gunnedah and Coonabarabran in the other. How far easterly these beds extend it is not possible to say. At many points in the State, Jurassic

sandstones weather easily to form sandy wastes, and this suggests that some of the low-lying areas composed of sandy wastes rising above the alluvium in the vicinity of Narrabri may represent Jurassic sandstones. However, there is no other evidence on which to base a determination of the age of the beds and it would be difficult to draw any satisfactory line of demarcation between the Triassic and what may be Jurassic beds. In the absence of any definite evidence of Jurassic strata in the area, the Mesozoic beds have all been shown as Triassic.

Tertiary Igneous Rocks.

They consist mainly of an alkaline suite of intrusives and extrusives and comprise porphyries, rhyolites, trachytes, andesites and basalts, together with a group of calcic rhyolites and basalts (Jensen, 1907). Tuffs and breccias are associated with them in places. The whole group of rocks has been described previously by Jensen, whose paper dealt mainly with their petrology.

The rocks occur as flows, dykes and sills, and often pass from one of these forms into another. The shape of the resulting igneous mass is complex and this, together with the abundant talus, which occurs on steep slopes, renders accurate mapping difficult and in some cases impossible. Mapping is further complicated by the occurrence of blocks of Triassic and Permian sandstone which have been "floated up" by the Tertiary intrusives.

Tertiary to Recent.

The only sedimentary deposits of these ages comprise alluvium and cemented gravels. The alluvium is largely of the "black soil" variety, although adjacent to the sandy wastes derived from the weathering of Mesozoic sandstones, it contains a fair proportion of sand.

The main development is along the Namoi River and in the Maules Creek-Bibbla Creek area. Very large alluvial areas lie north-west of Narrabri, beyond the limits of the area mapped.

STRUCTURAL GEOLOGY.

The boundary between the Carboniferous and the Permian beds is in the nature of a thrust fault. The zone of thrust faulting has now been traced continuously from the Werrie Basin (Carey, 1934), through the southern part of the County of Nandewar (Lloyd, 1933; Hanlon, 1948a), to the Nandewar Mountains.

The eastern thrust lies outside the area mapped and its exact location is a matter for conjecture. From a few scattered observations and the reported occurrence by Jensen (1907) of Devonian (?) cherts and slates near Waterloo Pinnacle in the Parish of Connor, County of Nandewar, it seems likely that the eastern thrust trends approximately parallel to the western thrust, which is shown on Plate XX, and passes close to Waterloo Pinnacle. North of this point there is little evidence on which to judge its position. It probably follows along or east of the spur which forms the divide between Maules Creek and the easterly flowing tributaries of the Manilla River. This spur parallels the western thrust and joins the Nandewar Range near Old Man Mountain. In the Parish of Lindesay, County of Nandewar, Raggatt (1931) recorded the occurrence of typical Burindi shales and conglomerates which extended eastwards to the divide, where they were covered with Tertiary volcanic rocks and westwards passed upwards into massive conglomerates, rhyolite and felsite (Rocky Creek Conglomerates.—F.N.H.). The structure was in the form of an anticline which was probably closed to the south. This would conform with the structure of the zone between the two thrusts further south, which is generally anticlinal.

The western thrust follows approximately a north-westerly trend, until it is obscured by the Tertiary igneous rocks. For most of the distance it is covered

by alluvium. It probably lies some little distance in front of the line of Carboniferous hills, because, where the coal measures outcrop and its position can be estimated with reasonable accuracy, this is the case. From the point between Black Mountain Creek and its tributary Basin Creek, in the Parish of Rusden, County of Nandewar, where the fault is obscured by Tertiary igneous rocks, it must swing away to the north. If it continued on a north-westerly trend it would cross Eulah and Bullawa Creeks and could not fail to be identified. Jensen (1907) recorded mainly trachyte with some sandstone on the western fall at the head of Bullawa and conglomerates (Rocky Creek conglomerates according to Benson (1917)) on the eastern fall at the head of Boomi Creek. It is probable that the fault follows along the range at this point, being covered by the Tertiary igneous rocks. Further north at Nobby's, in the Parish of Paleroo, County of Murchison, a fault again forms the boundary between the Carboniferous and the Permian and probably represents the continuation of the western thrust.

As to the age of the thrusting, all that can be said with certainty is that it is post-Lower Coal Measures. From a study of adjacent areas, it is clear that the thrusting post-dates the Upper Coal Measures. The upper limit to the age can be judged only from a consideration of general principles and it is proposed to leave the discussion of this point until a later date.

West of the zone of thrust faulting and away from the influence of any Tertiary intrusives or associated faulting, the dips are generally low and vary between south-westerly and westerly. This accounts for the change from Triassic to Permian beds as one proceeds up many of the westerly flowing creeks.

The relationship of the Triassic to the Permian appears to be that of a progressive overlap. In the Parish of Eulah, the basal Triassic conglomerate rests directly on the Upper Marine and the Upper Coal Measures, which form such prominent outcrops west of the Namoi River in the Boggabri and Gunnedah areas, are missing. Further east in the Black Mountain Creek area the Upper Marine beds were not recognized. In the north along a tributary of Bobbiwaa Creek, *Glossopteris*-bearing shales occur close to the base of the overlying Triassic beds, and it appears that the Upper Marine beds have been overlapped in turn.

Faulting was also associated with the intrusion of the Tertiary igneous rocks, and the faulting, combined with the "floating up" of masses of sediments on the Tertiary intrusives is considered to account for the occurrences of coal measures which lie above Triassic beds to the west. The Tertiary intrusions probably followed lines of weakness developed during the earlier folding and thrusting.

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SUMMARY.

The Permian outcrops comprise only the Lower Coal Measures and Upper Marine Series. The Upper Coal Measures are overlapped by the Triassic. Carboniferous beds have been thrust against the Permian along their eastern boundary. Widespread igneous activity in Tertiary times resulted in the intrusion and extrusion of a comprehensive group of alkaline rocks.

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NOTE ON THE OCCURRENCE OF TRIDYMITITE IN METAMORPHOSED HAWKESBURY SANDSTONE AT BUNDEENA AND WEST PYMBLE, SYDNEY DISTRICT, NEW SOUTH WALES.

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INTRODUCTORY.

It is well known that the Hawkesbury Sandstone, where penetrated by basic intrusions and volcanic vents, has been metamorphosed into quartzitic rocks. The degree of change varies greatly, so much so that in various occurrences all gradations from slightly indurated sandstone to almost completely recrystallized derivatives have been observed. It is rare, however, to find evidence of greatly elevated temperatures having operated in the contact metamorphic zone.

The nature of the metamorphism has not been thoroughly studied in any one locality, and little has been placed on record concerning the petrological details of the changes. Considerable reference has been made, however, to the megascopic structural features in the sandstone. Thus the prevalence of a prismatic shrinkage-structure has been commented upon and some occurrences have been illustrated and described in early geological papers.

It is clear from even cursory field-examination that two types of metamorphism have affected the Hawkesbury Sandstone :

- (a) Purely thermal (non-additive) metamorphism has been operative, causing the baking of sandstone with some mineralogical and textural modifications.
- (b) Addition of siliceous solutions has been associated with thermal change, contributing to the development of glassy, quartzitic derivatives.

DESCRIPTIVE.

The aim of the present note is to record the occurrence of *tridymite* in contact metamorphosed phases of the Hawkesbury Sandstone at Bundeena, near Cronulla, and at the road-metal quarry, West Pymble. During a recent visit with Mr. G. E. McInnes, Demonstrator in Geology, to the Bundeena locality, the author noted the rather unusual appearance of finely-textured prismatic quartzite which occurs immediately adjacent to a weathered basic dyke. The field-relations can be well studied at the locality of the Bundeena Ferry Wharf, which is served by launches from Cronulla.

Here the tectonic environment of the dyke-unit and the general metamorphic effects can be quickly perceived. It is clear that variable textural conditions of the original sandstone have contributed to selective silicification. Fuller treatment of the problems presented by these outcrops will be undertaken in the future.

The somewhat peculiar grey quartzitic rock has been studied microscopically. It contains a not inconsiderable amount of the somewhat rare mineral *tridymite*, a variety of silica.

The tridymite is found mainly in two ways:

- (a) As small laths and tabular crystals forming irregular fringes to quartz grains, and
- (b) as elongated crystals and tiny plates embedded in a partially glassy mesostasis.

In addition, some tridymite units are set in recrystallized potash feldspar, and radial-fibrous (partly spherulitic) material is occasionally present.

The tridymite is almost wholly in the inverted condition of quartz. This is to be expected in view of the known data concerning the stability-ranges of the various forms of silica. The small quantity of non-inverted tridymite shows very low D.R. (0.003–0.004) and extinguishes parallel to the length of the crystal or fibre. Wedge and arrowhead twinning is sparingly developed. The tile or imbricate structure of this mineral (as reported in literature) is not present. The refraction is low (approx. 1.47) but the bulk of the material shows the refractive index and birefringence of quartz.

The arrangement of the fringe-minerals is most erratic, and in many, but not all, cases the fringe and plexus-material extinguish at the same time as the quartz grains to which the tridymite is attached.

The glassy patches are mostly of feldspathic material, possessing a refraction greater than that of the pseudomorphed tridymite.

Some grains of quartz in the Bundeena rock have been completely recrystallized, producing aggregate-assemblages marked by very crenulated borders.

The rock from the contact in the Pymble quarry contains less tridymite than that from Bundeena, and this would appear to be related to

- (a) the temperature in the aureole during metamorphism having been lower, and
- (b) the original feldspathic content having been small.

This view is taken because careful study of the Bundeena rocks shows that partial vitrification of the sandstone is achieved by the formation of a feldspathic melt (with or without some added quartz). Such a melt has attacked the quartz grains with resulting solution leading to enrichment of the melt in silica. With fall of temperature the tridymite has crystallized in plates and rods embedded in yellowish or brownish glass.

Although the optical and crystallographic properties of the tridymite and of the inverted quartz are similar in the rocks of the two localities, a notable feature is that the extinction of rods and laths is not always straight (or parallel). One would expect straight extinction for quartz pseudomorphic after tridymite, if the elongation of the rods were parallel to the optic axis "c" of the quartz, or if the laths represented sections perpendicular to (0001 plates). The phenomenon of an inclined extinction of tridymite with angles up to 45 degrees puzzled Flett in his descriptions (1911) of buchite inclusions in a dolerite sheet in the Ross of Mull.

In the present investigation the tridymite-bearing rocks were taken from almost at the contact surface between dolerite and sandstone. Thin slices of a quartzitic rock taken about 30 feet from the contact in the Pymble quarry show no sign of tridymite.

GENERAL.

The present occurrences are in line with cases described from other parts of the world. Thus Harker (1939) has described and figured tridymite-bearing quartzite from the Torridonian Series of Rum, and his illustration (Fig. 21A) portrays exactly the manner of the occurrence at Bundeena. H. H. Thomas (1922) has described inverted tridymite fringes in buchite from Mull, and with

Hallimond (1920) has described the optical properties, stability-range and other characters of tridymite.

The fringe-structure of the tridymite at Bundeena and Pymble is exactly matched by the examples figured by Flett (1911) and Reynolds (1908).

Reflecting on the occurrence of tridymite in general one can stress that this mineral develops under two very differing environments: (a) that in which quickly elevated temperatures affect felspathic sandstones adjacent to basic intrusions; and (b) that in which late magmatic fluids, acting upon rhyolitic and trachytic lavas, bring about the eventual crystallization of tridymite plates, often in cavities.

It is thought by the author that this is the first record of tridymite in New South Wales, and it is proposed to make further field and petrological study of some of the contact-metamorphosed aureoles in the Hawkesbury Sandstone of the Sydney Basin. In a later communication fuller details and illustrations of the occurrence of tridymite will be given.

ACKNOWLEDGEMENTS.

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THE STRATIGRAPHY AND GENERAL FORM OF THE TIMOR ANTICLINE, N.S.W.

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INTRODUCTION AND GENERAL PHYSIOGRAPHY.

The Timor Anticline is developed in a belt of Devonian rocks in the Upper Isis River district about 16 miles north-east of Murrurundi, which is distant 218 miles by rail from Sydney.

It occupies the lower country south of the Liverpool Ranges, and the portion here described is the core of the fold as developed north of Timor Estate in the Parishes of Crawney and Lincoln, County Brisbane.

The Devonian belt here is a continuation of the Devonian rocks which lie to the south and south-west of Tamworth and Nundle, and which were described many years ago by Benson (1913–1918) in his Serpentine Belt series of publications.

The anticlinal structure is the southward continuation of a geanticline known to trend from west of Bingara and Barraba, through Manilla, and southward to west of Tamworth and Nundle. In the country south-west of Tamworth, this anticlinal zone is succeeded westerly by the Werrie Basin, described by Carey (1934).

The general physiography of the area may be summarized as follows :

The Isis River in the Timor district is in a late mature development, and to the north its headwater tract merges into rugged country of the foothills on the Liverpool Ranges, which shut in the valleys to the N.W., N and N.E.

The valley-floor, which, in the region described, is from 2,100–2,400 feet above sea-level, is not heavily alluviated ; however, notable aggradation of the river is seen further south between Timor and Waverley.

Between the present level of the alluvial plain and the high country of the Liverpool Ranges is a number of erosion levels which can easily be traced in the field. One of these is the old sub-basaltic surface which lies at an average elevation of about 2,700–2,800 feet above sea level. On this surface were

poured the Oligocene lavas. Surmounting the basaltic ridges are several peaks the highest and most spectacular of which is Wombramurra Peak (4,100 feet). These eminences alternate with gaps or passes, of which Crawney Pass (3,650) is the best known.

Since full physiographic details are not required in the present discussion, it is sufficient to note that pulsatory uplift of a basalt-covered peneplain led to the development of valley-in-valley topography, at least one erosion level being for the most part a revealed peneplain surface. Modifying the simple plan of valley-in-valley sculpture is the work of numerous subsequent tributaries of the Isis River. Remarkable adjustment between the detailed physiographic evolution and the geological structure is manifest everywhere in the area.

PREVIOUS WORK AND SCOPE OF THE PRESENT PAPER.

Practically no stratigraphical or structural investigation has been made upon the area. Carne and Jones, in describing the limestone (1919), drew attention to the presence of an anticlinal structure. Earlier references to the district are to be found in the record of fossils collected by Cullen (see Dun, 1900) and the description of *Endophyllum schlueteri* by Etheridge (1898). A cryptic reference by Phillips (1875) no doubt refers to the Crawney limestone in County Parry. Benson (1918, 1922) gave lists of fossils from the Isis district and from the large deposit of limestone on Wombramurra Creek, north of the Liverpool Ranges, which may be the continuation of the Isis belt. A study of the Wombramurra outcrop is most desirable.

The first-named author of the present paper determined the existence of the anticline independently, and intermittently over several years mapped the area, in great detail, completing the field work in 1942. In 1945 he supervised further detailed investigation and check-mapping by the other authors. The results of the work are embodied in the map (Plate XXII), which is intended to show the salient structure.

The present paper deals with the general stratigraphy and summarizes the morphological features of the anticline. The stratigraphy has been dealt with only as an aid to the structural studies.

The genetic aspect of the structural features contributes to a study of tectonic evolution of the Hunter-Manning Province now being completed by Osborne.

STRATIGRAPHY.

Rocks of Middle and Upper Devonian age are exposed in the valley of the Isis and its tributaries. The higher ground is given over to basalt flows with occasional plugs, sills and small sills of dolerite; these are all of mid-Tertiary age.

The chief feature of the stratigraphy is the existence of a large mass of limestone, richly fossiliferous in corals, brachiopods and hydrozoans. This limestone (here named the Timor Limestone) is to be correlated with part of the Moore Creek sequence of the Tamworth and Attunga districts, which has been fully investigated by Brown (1942). We are indebted to Dr. Brown for having checked the fossil-horizons of the Timor Limestone.

The limestone is underlain by tuffs, conglomerates, banded cherty-claystones with slump bedding and intraformational brecciation, thin spilite flows and breccias, and thin dolerite sills. Many of the fragmental rocks are fairly high in soda content. The rocks overlying the limestone comprise tuffs, conglomerates and banded tuff-claystone units.

It is clear from geographic and structural relationships between the Timor area and the Serpentine Belt province to the north that the rocks of the anticline

are definitely the equivalents of portions of the Tamworth and Barraba successions, including probably the Baldwin Agglomerates (which form the lower portion of the Upper Devonian sequence).

The limestones vary in thickness, but reach a maximum of 760 feet in the neighbourhood of "Allston" Station. Much of the surface of the country within the central part of the anticline is given over to limestone or to subordinate calcareous shaley beds so that the map displays a wide core of limestone (Plate XXII).

In mapping the main fold and also the smaller structures (see below), considerable help was afforded by the zonal character of the limestone succession. Distinct fossil zones were noted (more from the presence of one or two prominent genera than from any marked zonal assemblage), and the recognition of these zones helped greatly in delineating the structural detail in complicated areas. This was especially true of the Glen Dhu complex.

The persistence of a rhythmically banded shale-limestone zone at the base of the main mass, and of a cherty silicified and cavernous zone at the top of the mass, further expedited the structural mapping. In effect, various fossiliferous zones became reliable tectonic indicators in areas of faulting.

It is proposed to state the generalized sequence of the area with special reference to the limestone.

Descending stratigraphically, we have :

	Maximum Thickness in Feet.
Barraba Series—	
Mudstones with bands of fine grained tuff and frequent <i>Lepidodendron Australe</i> and <i>L. Osbornei</i> . Occasional layers with <i>Radiolaria</i>	300
Fine tuffs with angular and rounded pebbles in acid matrix (Baldwin Agglomerate type)	50
Tamworth Series—	
Banded tuff-chert material	100
Fine claystones	200
Well bedded tuff-chert material	250
Tuff-chert layers with intrusive tuff	80
Coarse albitic breccia	100
Blue fine tuff	80
Conglomerate abruptly changing in texture	150
Blue tuff and coarse breccia	80
Blue-green keratophyric tuff	120
Tuffaceous chert with <i>L. Australe</i>	180
Tuffs with some intraformational complications	90
Evenly bedded mudstones with <i>L. Australe</i>	80
The Timor Limestone—	
Siliceous, sometimes agatized, cavernous limestone :	90 ft.
<i>Horizon 8.</i> Glen Dhu zone of corals including <i>Tryplasma</i> : 120 ft. from top.	
<i>Horizon 7.</i> <i>Endophyllum</i> zone :	175 ft. from top.
<i>Horizon 6.</i> <i>Pachypora</i> abundant :	225 ft. from top.
<i>Horizon 5.</i> Gastropods abundant :	280 ft. from top.
<i>Horizon 4.</i> <i>Amphiphora</i> , <i>Favosites</i> and rugose corals abundant :	300 ft. from top.
<i>Horizon 3.</i> Stromatoporoids abundant (Allston Zone) :	550 ft. from top.

Horizon 2. Heliolites Zone: 570 ft. from top.

*Horizon 1. Brachiopods (including rhynconellids)
abundant: 590 ft. from top.*

Blue limestone: 90 ft.

Rhythmically banded shale-limestone with characteristic
dark-red or black soil (Trilobite recorded at base):
80 ft.

<i>Total limestone</i>	760
Chert-tuff strata with intraformational disturbances (Tamworth facies)	50
Tuffs and cherty-claystones	145
Tuffs with alternating coarse and fine grain	150
Well-bedded blue-green cherts	40
Agglomerate with spilitic and limestone fragments	10
Chert-claystone and shale-breccia	135
Green keratophyric tuffs with quartz veins	50
Claystones (Tamworth type)	20
Tuffs and claystones	100
Blue-green tuffs and albitic tuff	35
Spillite	10
Hard resistant tuff bar	10
Blue cherts	60
Spillite flow	15
Cherts and tuffs (with some silicification)	245
Well-bedded tuff	20
Breccias alternating with fine tuff, containing <i>crinoid</i> .	
Hard blue tuffs with cherty fragments	25
Shaley mudstones 20 ft. exposed. (Base of the Tamworth Series not encountered)	20
Total of section	3,760

REGIONAL DISTRIBUTION.

The limestones are confined to an area, partly rectangular, of approximately seven square miles. The general trend of this area, which is three miles wide, is N. 20° W., this being the main direction of strike of the rocks. A little to the south of Isaacs Creek the southernmost tip of the anticline is seen in portion 65 (Parish of Crawney), but soon the outcrop widens and swells northward and eastward into the heart of the fold. This broad development of limestone continues several miles to the valley of Dead Eye Creek, where thrusts cut across its northern margin.

From portion 78, Parish of Lincoln, to the north only a narrow outcrop of limestone is present. This runs parallel to the Isis River and parallel to the Crawney Road, and here has a steep dip (48°) to the west. Eventually this narrow belt dies out just north of the parish boundary (Crawney-Lincoln) near Oakey Creek.

Lying east of the main outcrop, at its southern end, is an isolated sector of limestone. This is well-exposed in the country immediately north and south of the headwaters of Isaacs Creek. Faults separate it from the main anticlinal limb.

On the west side of the Isis from Glen Dhu to a little south of Isaacs Creek, the structure is continuous, possessing a dip varying from 15–20° in the direction W. 20° S. Fairly constant strike is maintained, as also is the thickness, viz. 760 feet. The limestone has markedly determined the physiographic conformation in this locality.

Small outcrops of limestone, especially of the coralline Glen Dhu zone, are found in the valley of Dead Eye Creek, and considerable faulting and structural complexity are responsible for the general distribution here.

The rocks of the Tamworth Series which underlie the limestone are not exposed sufficiently to permit satisfactory study. They are found in creeks in the central part of the area, especially along the axis of the anticline, e.g. in Perry's Creek.

The Tamworth Series, which succeeds the Timor limestone, is best studied in the eastern portion of Isaacs Creek and south thereof in Branch and Double Creeks. In these latter streams one notes the large development of albitic tuff and considerable amounts of the characteristic tuff-chert sediment with contemporaneous disturbances.

The Barraba mudstones and the limited Baldwin Agglomerate are found flanking the limestone on both sides, and succeeding it southward in the direction of plunge.

The fact that there is a much greater development of Tamworth strata in the southerly pitching nose-area of the anticline, as compared with the flanks of the structure, suggests that some erosion of the supra-limestone strata took place before the Upper Devonian sediments were deposited. The important implication of these data is briefly treated within the next section.

STRUCTURE.

Relations of the Tamworth and Barraba Series.

This matter has been carefully examined in the field. In one place in Upper Isaacs Creek a slight angular unconformity is demonstrable, by noting the dip and strike relationships. Elsewhere in the country between Branch Creek and to the N.W. and N.E. the Barraba Series transgresses the *Tamworth* Series only very slightly. The fact that the anticline is plunging makes difficult the investigation of problems relating to structure. A point bearing on the question, however, is that of the evidence of compaction and diagenesis; in the Tamworth Series physical processes have developed to a much greater degree than in the Barraba rocks. Further, the latter are free from quartz veins which are found in the former. This suggests a lapse of considerable time between the periods of sedimentation. Yet again is the testimony of minor structures in the Tamworth Series which imply the operation of stresses prior to Barraba deposition.

Therefore it seems justifiable to assume a time-break between the two series, and to postulate the progress of some crustal warping with attendant contemporaneous erosion in this area.

The Timor Anticline.

This structure is best designated an anticline although in point of fact the limestone outcrop almost completely closes so as to produce a dome-like unit. The closure on the north is due to thrusting which has bent down the axial zone of the anticline and delimited the central structure in that direction.

The fold is seven miles long and approximately three miles wide. The general strike is N. 20° W., but some swinging of the whole arch is clearly detectable. The axis of the fold, as plotted in many cross sections, bears out the swing (see map).

The anticline is essentially a flat-topped arch with marginal dips of 25–28° on the west, and to the east a maximum of 51°. Its cross-section is simple in the broad sense, but many interesting minor features occur, which have important structural significance. The minor tectonics of the area are admirably displayed for demonstration.

Chief amongst the minor structures (most of which will be genetically discussed in another paper) are :

- (a) A trough-faulted rift cutting obliquely across the main axis. This is developed N.E. and S.W. of Perry's Creek. Tensional fractures prominent here.
- (b) A stair-case-like cross fault system developed athwart the central part of the rift.
- (c) Several sharp synclinal crumplings, and two miniature anticlinal crumplings of great sinuosity. Also a number of thrust (quasi-imbricate) zones with combinations of both plastic deformation and shattering.
- (d) On the south-plunging nose of the fold are several minor contortions (seen well about the lower Isaacs Creek area.) These imply the structural weakness of the limestone when heated by the effects of severe deformation.

Some further details may now be given concerning the structures of (a) and (b), although more will be said in a later communication.

The rift breaks obliquely across the crestral zone of the region, and is more or less meridional in its trend. It has torn the limestone open by the operation of two longitudinal tensional faults, and differential block-faulting has occurred within the zones bounded by these fractures. The limestone, in several of these minor block-units within the trough, has been displaced through considerable relative vertical distances, e.g. up to 100 feet. The trough-fault in Perry's Creek lies in this category, since a little to the south of the creek the first ridge is capped by a restricted area of basal beds of the limestone. This small outcrop represents the continuation of the Perry's fault-trough, the vertical displacement being much less than that recorded in Perry's Creek. Further, in the case of the cap we find that the limestone in contact with the bounding faults has been rotated by the frictional drag, producing a saucer-shaped structure in limestone. This same trough extends in a northerly direction and an examination of the structures in the area indicates a differential movement of blocks within the zone of fracture.

Faults other than Minor Examples.

The faults which are present may readily be classified into :

- (a) Tensional faults of the valley floor and of the eastern margin of the anticline.
- (b) Parallel thrusts of the Glen Dhu complex.

(a) These comprise three meridional fractures : one trending along the line now occupied by the river, and the other two forming a senkungsfield in the eastern Isaacs Creek sector.

The meridional fault (to be called the Isis Fault) begins in the north at the junction of Perry's Creek and the Isis River, and strikes approximately S. 30° E., increasing in downthrow southward.

This predetermined line of weakness has not always been the site of the river bed, for studies of the physiographic evolution make it clear that the river originally occupied a subsidiary anticline (now east of the Isis) and in course of its development migrated westerly along the limb of the anticline into the fault-zone where it has entrenched itself to some degree. The fault has given rise to marmorization of the limestone near the road-bridge over the river, about one mile north of Isaacs Creek.

The trough on the eastern side of the area is complicated by the existence of small cross faults within the walls of the senkungsfield. There are some steep dips and corrugations in the beds adjacent to the faults, while within the trough an exotic band of limestone indicates by its differential movement and

variable positions that considerable complexity has marked the movement of the blocks.

It would appear that the tensional structures so far described, developed during periods of stress-relief associated with and following the main deformation which produced the anticline.

(b) The full account of the thrusts and associated features at Glen Dhu are reserved for genetic discussion in the work now being produced by one of us (G.D.O.). It will be sufficient to summarize the structural development here by saying that succeeding the main folding which produced the geanticline between Bingara (in the north) and Dungog (in the south) there was superimposed a system of forces, chiefly related to a southward or south-eastward thrusting and some rotational stresses. These brought about the development of faults trending N.N.E. and S.S.W. This north-north-west stress caused some flexuring of the axial zone of the anticline, thus shortening the fold in the crestal direction.

AGE OF THE STRUCTURES.

From correlation of the Isis area with other areas whose geological history is fully known we are of the decided opinion that all of the deformation took place in the Hunter-Bowen diastrophic cycle. The Timor Anticline suffered some special stress conditions within that diastrophism, and received its closure then.

SUMMARY.

In the foregoing pages an account is given of the Timor Anticline, stress being laid on the structural features. It is shown that the Isis River district occupies an important place in the tectonics associated with the gradual unfolding of the Upper Palaeozoic formation. The stratigraphy has been dealt with fairly fully, and zone fossils are listed for the Timor limestone, which forms the basis of the tectonic study, being, as it is, the main datum for all structural investigations in the area described.

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THE GEOLOGY OF THE CANOWINDRA DISTRICT, N.S.W.

PART I. THE STRATIGRAPHY AND STRUCTURE OF THE CARGO-TOOGONG DISTRICT.

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With Plate XXI and two text-figures.

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I. INTRODUCTION.

The district geologically mapped and described in this paper lies to the north of Canowindra and to the south-west of Orange. Cargo and Toogong are the chief localities within the area, and are both about 200 miles from Sydney by road.

The area studied is of approximately 330 square miles; bounded to the west by the Mandagery Range and Nangar Mountains, and to the east by the Black Rock Range.

Towards the close of the last century extensive gold-mining operations were carried out at Cargo and Burdett. Brief accounts of the geology of the Cargo goldfield have been given by Hutton (1875), Wilkinson (1878) and Anderson (1890). In 1915, Andrews and Morrison carried out a geological survey of the immediate vicinity of Cargo, their purpose being to revive interest in this mining field.

Limestones near Cargo and Cudal have been reported upon by Carne and Jones (1919), and some of the outcrops are shown on their maps.

The geology of the country adjoining the north-west section of this area has been described by Joplin and Culey (1937); and Sussmilch (1906) has noted the stratigraphy of the Silurian and Devonian rocks in the parish of Barton, adjoining the north-east section of the district.

II. PHYSIOGRAPHY.

Taken as a unit, the district is undulating to hilly, showing a stage of late maturity in the erosion cycle. The elevation above sea level varies from that of the Orange-Blue Mountain plateau (3,000 feet) to the level of the Lachlan-Belubula valley (1,000 feet).

Along the eastern and western sides of the area examined are prominent quartzite ridges with meridional trend, rising 600 to 1,000 feet above the surrounding country, which is undulating, with a general slope from the north-east (near Mt. Canobolas) to the west and south.

The gradual slope is interrupted by a low, east-west watershed, extending from Columbine Mountain to Burdett. To the north, the district is dissected by the Mandagery-Boree drainage system, while to the south, streams enter the Belubula River, either separately or by way of Canomodine Creek. Both Mandagery Creek and the Belubula River flow into the Lachlan River, but follow widely different courses.

The main streams of the Mandagery-Boree drainage system rise in the Lachlan-Macquarie divide and in the Canobolas Mountains, and flow in a south or south-westerly direction towards Toogong. The creeks follow meandering courses, for the most part between banks of alluvial deposits 12 to 20 feet high.

South of Cudal, flows of Tertiary basalt follow the valleys of the present-day streams, preserving old alluvial deposits. The streams have been rejuvenated, cutting steep-sided gorges up to 50 feet deep through the basalt.

A few miles south-west of Toogong, Mandagery Creek loses its aspect of late maturity as it leaves the gently undulating country and flows through a gap in the resistant quartzites of the Mandagery Range.

Most of the creeks on the south side of the east-west watershed join either Nyrang or Canomodine Creeks. These become progressively more youthful towards the east, depending mainly on an increasing gradient in this direction. Canomodine and Four Mile Creeks rise near Mt. Canobolas and flow in a southerly direction to enter the Belubula River. Like Mandagery Creek, they have cut deep gorges through the quartzites, but their average gradient is steeper. They are not associated with large areas of gravels, and are relatively youthful compared with Mandagery or Boree Creeks.

The undulating country between the bordering quartzite ranges consists mainly of slates, lavas, pyroclastic rocks and limestones, invaded by porphyry and partly covered by basalt flows.

Certain of these rock types are much more resistant to erosion than others, and give rise to prominent ridges which parallel the strike of the beds (e.g. the phyllites west of Mandagery Creek, the coarse tuffs and breccias west of Cudal, and the crystal tuffs south of Cargo). Between Burdett and Barragan, the rock types are mainly porphyry and slate. The slates are more resistant and form long, parallel ridges; the valleys between the slate ridges are broad and mature.

The courses the streams follow are dependent partly on rock type and partly on directions of jointing and faulting. Canomodine Creek and one of its tributaries flow along fault zones on either side of Columbine Mountain, and the former creek also follows the strike of a fault near Canomodine Station. The alluvium of Oaky and Boree Creeks conceals a fault near Toogong.

Several of the creeks follow the strike of the beds for some part of their length, notably Mandagery, Four Mile, Cargo and The Grove Creeks. Jointing is largely responsible for the minor deviations in the stream courses.

At Gum Flat, near Cargo, there is an exceptional thickness of Tertiary or Pleistocene sediments, covered by Recent alluvium. Shafts indicate a maximum thickness of 370 feet of clays and gravels. Boulders of Upper Devonian quartzite

occur in the deeper levels, but this rock does not outcrop in the present restricted catchment and must have been derived from the quartzite ridges to the east. Consideration of the levels of the base of the Gum Flat sediments as revealed by mine shafts and surface boundaries shows that the slope of the old valley floor is from south-east to north-west, consequently it is probable that there has been a reversal of drainage. The old stream had its source in the quartzites south-east of Cargo, flowed west across the low divide between Canomodine and Cargo Creeks, then north-east past Gum Flat, to join Cargo Gully and Gerybong Creek.

At a later stage, due probably to local subsidence, prolonged alluviation took place. The lower part of the present Canomodine Creek then began to cut back in a northerly direction and capture the headwaters of the old Gum Flat stream. It seems likely, therefore, that the headwater tract of Canomodine Creek originally emptied into Gerybong Creek, by way of Gum Flat.

Evidence of the former course of an old stream lies in the occurrence of a patch of large, water-worn boulders high up on the eastern side of the valley of Canomodine Creek, south-east of Cargo.

As a result of the river capture noted above, and the consequent reversal of drainage, a watershed was set up in the alluvium of Gum Flat, west of Cargo, and the creeks assumed their present directions of flow.

III. STRATIGRAPHY.

The greater part of the stratified and effusive rocks belong to the Older and Middle Palæozoic era; a minor part of the area is covered by Tertiary lavas and Cainozoic alluvial deposits.

(1) Ordovician.

The oldest rocks outcropping in the district are of Upper Ordovician age. They are black, banded slates and cherts, with well-marked laminae which show differential weathering, giving a distinctive appearance. The rocks occur in two small inliers bounded by faults, three miles east of Cargo. They are highly folded, with approximate meridional strike.

Their Upper Ordovician age has been established by the finding of the following graptolite fossils in portion 98, Parish of Cargo:

- Diplograptus* cf. *truncatus*.
- " cf. *rugosus* var. *apiculatus*.
- " cf. *quadrimucronatus*.

Cf. *Retiograptus* sp.

Dicellograptus sp. (perhaps allied to *D. pumilus*).

Cf. *Lasiograptus harknessi* var. *costatus*.

These graptolites have been determined by Mrs. K. Sherrard, M.Sc.

(2) Silurian.

Strata of this age occupy the greater part of the area mapped. The sequence varies somewhat over such a large district, but a generalized succession is shown in Table I, where it is correlated with that of the Molong-Manildra (Joplin and Culey, 1937) and Wellington (Basnett and Colditz, 1945) districts.

(i) *The Lower Sedimentary Series*. Rocks which appear to underlie the Cargo Andesitic Series (and thus to belong to a horizon equivalent to the Lower Sedimentary Series of the Wellington district), occur six miles south-east of Cargo. They are bounded on the east by a fault junction with Upper Devonian quartzites, and appear to dip under the andesites to the west.

The rocks are blue-grey and reddish slates, passing upwards into beds of slates and fine tuffs. These are overlain by a limestone, the topmost bed of the series.

(ii) *The Cargo Andesitic Series.* The members of this series outcrop in two belts belonging to the same series and repeated by folding. The larger area exposed is in the Cargo district, where the series is four miles wide, due however, to complicated folding and faulting. The smaller belt extends almost north-south, through Barragan, to the west of Cargo.

The series consists of a great variety of andesites, trachyandesites, basalts, tuffs and breccias, with interbedded clay slates, cherts and occasional limestones.

TABLE I.
Correlation of Silurian Stratigraphy.

Cargo-Toogong.	Molong-Manildra.	Wellington.
7. Rhyolites. 6. Slates. 5. Canomodine limestone. 4. Slates and tuffs. 3. Cargo Creek limestone. 2. Cargo Andesitic Series. 1. (?) Lower Sedimentary Series.	5. Rhyolites. 4. Manildra beds. 3. Molong beds. 2. Andesites. 1. Limestone (Molong).	3. Upper Sedimentary Series. 2. Volcanic Series. 1. Lower Sedimentary Series.

It has been found inadvisable to map individual flows, slate or tuff beds within the series, because of their narrow surface outcrop and lateral variation. North and north-east of Cargo, mapping is hindered by soil cover, but good exposures occur in the country to the south-east, which has been dissected by Canomodine Creek and its tributaries.

A composite sequence, deduced from these exposures, is as follows :
(Cargo Creek limestone).

10. Tuffs.
9. Augite hornblende andesite.
8. Breccias, tuffs, cherts.
7. Amygdaloidal basalt.
6. Porphyritic trachyandesite (with large amygdules).
5. Augite andesite.
4. Trachyandesite or keratophyre.
3. Thin limestone bed.
2. Breccias, and andesites with xenoliths.
1. Cherts and slates.

All of these beds are discontinuous and the complete sequence will not be found in any one section.

The cherts and slates which appear to be the oldest strata outcrop in an anticlinal crest on Canomodine Creek and may belong to the Lower Sedimentary Series. Overlying these are dark grey-green breccias, and andesites containing rounded xenoliths like those near Wellington (Colditz, 1947). In places, a thin limestone bed follows ; usually devoid of fossils and somewhat marmorized.

The trachyandesites or keratophyres next in the sequence do not occur in the Canomodine Creek succession, but outcrop nearer Cargo. They are light grey, amygdaloidal rocks with small felspar phenocrysts in a holocrystalline base. New Chum Hill (west of Cargo township) is composed of this rock, and a similar type outcrops north and south-east of this locality. To the north, the keratophyres have been metasomatized by iron-bearing solutions, and appear as black, fine-grained amygdaloidal rocks.

On Canomodine Creek and to the south, the next horizon is that of a greenish andesite with pink felspar phenocrysts. Aggregates of calcite seen under the microscope indicate the former presence of augite.

Towards the eastern side of the Andesitic Series on Canomodine Creek, porphyritic trachyandesites outcrop, followed by a fairly persistent band of coarse breccias. The stratigraphical position of these rocks is a little uncertain, as they are separated from the preceding strata by a fault, and do not occur on the south-western side of the series.

The trachyandesites vary slightly, but most are characterized by large phenocrysts of pink or cream plagioclase. In some localities they are markedly amygdaloidal, the calcite amygdules attaining a diameter of 35 millimetres.

The breccias are generally coarse, grey-green rocks, containing large angular fragments of andesites and cherts. They are well-stratified, and near the top of the sequence are interbedded with cherts and reddish clay shales. The latter underlie a limestone which will be taken as the equivalent of the Cargo Creek limestone, the bed which marks the top of the Andesitic Series. Breccias similar to those noted above are widespread around Cargo, especially in Copper Gully.

Along Canomodine Creek, on the south-west side of the Andesitic Series, the sequence is different. The augite andesite (5) is interbedded with tuffs and overlain by a thin flow of amygdaloidal basalt. An andesitic breccia with a matrix of calcite follows, and is possibly equivalent to some of the breccias which overlie the porphyritic trachyandesites. The topmost lava in this locality is an augite hornblende andesite with phenocrysts of tabular plagioclase closely packed together.

Most of the area north and east of Cargo is occupied by an andesitic lava with phenocrysts of cream plagioclase and occasional augite in a fine-grained black groundmass. The phenocrysts usually have a glomeroporphyritic arrangement, and the base is mainly of felspar and magnetite needles showing a variolitic structure. It is not clear whether this rock has suffered metasomatism or devitrification. A similar type from the Wellington district has been described (Colditz, 1947) as a devitrified glassy augite andesite. It occurs at the base of the Volcanic Series, which is in keeping with the position of this rock in the Cargo district.

It may also be pointed out here that the succession in the volcanic series of Cargo and Wellington shows other similarities, such as the presence of augite hornblende andesite and volcanic agglomerate near the top of the series.

Approximately parallel to, and four miles west of, the Cargo Andesitic Series, is an equivalent series, occupying the core of an anticline. The northern extension is terminated by a fault; the beds continue south for seven miles, and then plunge beneath overlying tuffs and slates.

The series has not been exposed to as great a depth as that of Cargo, so that only the uppermost beds outcrop. The oldest of these rocks occur in the centre of the fold near the northern end. They are dark, grey-green augite hornblende andesites resembling those near the top of the Cargo Series. These are overlain by coarse andesitic breccias, which consist of sub-angular fragments of augite andesites, cherts, etc., in a tuffaceous matrix rich in calcite, some of which is stained pink.

(iii) *The Cargo Creek Limestone.* This bed directly overlies the Cargo Andesitic Series, and is best developed along Cargo Creek three miles south of Cargo, where it outcrops continuously for four miles, with an apparent maximum thickness of 3,000 feet. Strike faulting, however, may have increased the width of outcrop.

The limestone is massive, with few shaley beds, and fossils are not abundant. *Favosites*, *Heliolites*, *Tryplasma* and *Pentamerids* (probably *Conchidium knightii*) have been found.

North-west of Cargo several small limestone lenses outcrop, separated from the Andesitic Series by tuffs, cherts and slates. They contain *Halysites*, gastropods and bryozoa. These limestones are probably of the same horizon as the Cargo Creek belt. In the south, continuous formation of limestone took place, while further north volcanic and marine conditions predominated.

The limestones near the Canangles Road, three miles south-east of Cargo, seem to be equivalent to the Cargo Creek belt. North of the road the limestone occurs in a syncline, plunging to the north-west; its north-westerly extension being terminated by a fault. South of the road the limestone again outcrops, having the structure of a south-plunging syncline, but the eastern limb of the fold is cut off by a fault, bringing the limestone in contact with Upper Devonian rocks.

These limestones are somewhat more fossiliferous than the main belt. The basal beds on the west side of the northerly-plunging fold contain small Rhynchonellids, while on the eastern side a brachiopod resembling *Stropheodonta* is present in a reddish-coloured marble. Higher up in the limestone *Heliolites*, *Tryplasma*, Pentamerids, Stromatoporoids and (?) *Favistella* have been found.

Near Barragan, limestone of the same horizon overlies the Andesitic Series, but is not well developed, occurring in isolated lenticular beds, mainly along the eastern margin of the breccias.

North of the Oak Creek fault and north-west of Cudal, the limestones do not directly overlie the Andesitic Series, but are probably of the same horizon. Here the andesites would again occur in the core of an anticlinal fold, but have not yet been exposed by erosion. In these limestones *Favosites*, *Tryplasma*, *Halysites*, *Pachypora*, Pentamerids and bryozoa have been found.

(iv) *Tuffs and Slates*. South of Cargo a series of crystal tuffs with inter-bedded cherts and slates overlies the limestone of the Cargo Creek belt.

The crystal tuffs are best developed in the southern parts of the area, notably between Cargo Creek and the Belubula River and east of Lockwood. These two occurrences are equivalent; situated on the east and west sides, respectively, of a syncline. Proceeding north along the strike of the beds, the tuffs become finer in grain-size and pass into cherts and claystones.

The tuffs on the north-west side of Cargo Creek are dark, fine-grained rocks, some resembling basalt in hand specimen, others showing spheroidal weathering or traces of bedding. Under the microscope, crystals of plagioclase, quartz, orthoclase, augite and brown hornblende are seen.

Towards the upper part of the series, slates predominate over tuffs, except between Canomodine and the Belubula River, where coarser tuffs are inter-bedded with the slates.

The maximum thickness of this series of tuffs and slates is about 5,000 feet.

In the Cudal district the equivalents of the Cargo Creek limestone are overlain by slates, then by pyroclastic rocks ranging from cherts to coarse breccias. These, together with the overlying slates, make up the "Manildra beds" of Joplin and Culey (1937), the slates and limestones being grouped together as the "Molong beds". The pyroclastic rocks may be correlated with the crystal tuffs south of Cargo. The breccias are best developed near Manildra, but thin out to the south, passing into tuffs, cherts and claystones.

Two thin limestone beds occur in this pyroclastic series north-west of Cudal, and in portion 52, Parish of Cudal, fossiliferous limestone overlies a breccia which is also rich in fossils. *Favosites*, *Heliolites*, *Tryplasma*, *Syringopora*, *Mitocystis*, *Orthosina* (?), Stromatoporoids, crinoid stems and bryozoa are present. In addition, *Dalmanites* and *Mucophyllum* have been previously recorded from this locality (Joplin and Culey, 1937).

This horizon is traceable to the south through "Derowie" (east of Toogong) to the cross-roads three miles south-west of Barragan. Small lenticular patches of limestone outcrop at these places, and near "Derowie" a compact crystal

tuff is interbedded with slates which overlie the limestone. *Halysites* and *Favosites* are present in the limestones.

(v) *The Canomodine Limestone.* This thick mass of limestone appears to overlie the tuffs and slates four miles south of Cargo. The belt has a maximum width of outcrop of two miles, due to folding in a synclinal structure.

On the western boundary, in the vicinity of Barrijin Trigonometrical Station, the limestone dips off a lenticular mass of andesites, andesitic breccias and tuffs. These beds do not appear on the eastern side of the syncline.

The Canomodine limestone is very massive and relatively unfossiliferous, resembling the Cargo Creek limestone. Carne and Jones (1919) infer that these limestones are of the same horizon, but examination of the area between these beds shows that the two limestones and the intervening beds (tuffs and slates) dip in the same direction (south-west), so that the Canomodine limestone is stratigraphically above the Cargo Creek bed, unless a major strike fault be postulated at the junction of the slates with the Canomodine limestone. No evidence of such a fault has been found, however.

The Canomodine limestone thins out rapidly to the north of Barrijin Trigonometrical Station, but an isolated outcrop in portion 176, Parish of Toogong, north of the Nanami Lane, is possibly of this horizon. There, the limestone has been partly silicified and jasperized; it contains abundant fossils, including *Halysites*, *Favosites*, *Heliolites*, *Tryplasma*, *Mucophyllum*, Stromatoporoids and bryozoa.

The limestone previously described as occurring interbedded with the breccias west of Cudal may be of this horizon.

(vi) *Slates.* Slates which overlie the Canomodine limestone outcrop in the synclinal structure between Avenel and Barragan, and those overlying the "Manildra" breccias may be noted here. At the last-named locality, some of the slates occur in an extensive shear-zone, and have been converted to phyllites. These rocks are traceable south along the boundary of the Upper Devonian strata as far as Burdett, where they are surrounded by porphyry.

(vii) *Rhyolites.* Rhyolitic lavas overlie the slates and phyllites and underlie Upper Devonian quartzites six miles west of Cudal. The lavas become more extensive to the north near Meranburn, where they have been noted by Joplin and Culey (1937). To the south they thin out and disappear two miles south of Dulladerry Creek, but an isolated outcrop occurs at Burdett.

The basal flows are white and purple rhyolites, with small phenocrysts of quartz and felspar in a felsitic groundmass. Succeeding lavas are mainly banded rhyolites; some spherulitic types are interbedded.

The banded rhyolites show excellent flow structure with local contortions; the colour varies from pink to pale green, with purple bands. Phenocrysts of quartz and altered felspar are present.

The lavas show evidence of silicification, and some mineralization, as phenocrysts are often replaced by quartz, and less commonly by pyrites, which has mostly been altered to hematite.

The age of these lavas is thought to be Upper Silurian, as a spherulitic rhyolite is interbedded with the slates which underlie the main lava flows. These slates do not resemble the typical Garra (Lower or Middle Devonian) beds, and are probably Upper Silurian.

Sussmilch (1906) has described rhyolitic lavas from the Parish of Barton (on the Cargo-Orange road), and places them at the top of the Silurian sequence.

(3) *Upper Devonian.*

Rocks of Upper Devonian age occur as long, meridional-trending belts on the eastern and western sides of the district, lying about 15 miles apart. They may be divided into an Upper and a Lower Series.

The Lower Series has restricted distribution, occurring in an anticlinal structure north of the Black Mountain (Fig. 2). It consists mainly of chocolate and green shales and mudstones. On Paling Yard Creek, a variety of *Lepidodendron* has been found in a green tuffaceous mudstone.

The Upper Series is well developed on both sides of the district. The main rock types are quartzites and sandstones, with some interbedded grits and red shales. These rocks make up the rugged country of the Mandagery Range and Nangar Mountains to the west, and the Columbine and Black Mountains, and the Black Rock Range on the east.

The quartzites vary from white to yellow or brown, and have resulted from silicification of arenaceous sediments during folding. Ripple marks, current bedding and worm burrows are present, indicating shallow-water deposition, but no fossils have yet been found in the district mapped. However, Sussmilch (1906) noted the occurrence of *Rhynchonella pleurodon* and *Spirifer disjuncta* on Spring Creek, eight miles north-east of Cargo.

The red colour of the shales changes to green along joints and watercourses, due to the leaching of iron compounds. In the gorge of Canangle Creek and further south, an impure limestone occurs in thin bands in the quartzite series.

The quartzites are overlain by red shales, followed by conglomerates. The latter have been mapped together with rocks of Lower Carboniferous age, and will be described below.

(4) *Lower Carboniferous.*

Rocks of definite Carboniferous age outcrop east of Columbine Mountain. They are greenish mudstones grading into tuffs of fine to medium grain-size. They contain abundant plant stems and at least two species of *Rhacopteris*.

The better-preserved species is allied to *R. petiolata*, a fern which occurs at the top of the Tournaisian in Great Britain, equivalent to the top of the Lower Kuttung of N.S.W. The other species is more like *R. inequilatera*.

The Carboniferous sediments appear to rest conformably on the Upper Devonian strata, and in the absence of a structural break the boundary should be placed at the base of the conglomerate noted above.

If this conglomerate is taken as Lower Carboniferous, rocks of this age exist over quite a large area, making up most of the undulating country between Columbine Mountain and the Black Rock Range, and extending south to the Belubula River.

The conglomerate is quite a compact rock of a purple-brown colour, containing pebbles of quartzite. Most of the tuffs and mudstones are difficult to split along the bedding, show spheroidal weathering, and sometimes contain spheroidal concretions.

(5) *Tertiary.*

The most important rocks of Tertiary age are the basaltic and trachytic lavas which have issued forth from the volcanic centre of Mt. Canobolas. The trachytes occur within a distance of eight miles from Mt. Canobolas, but the basalts, having a much higher degree of fluidity, have flowed much further down old river valleys in a south-westerly direction towards Toogong and Long's Corner.

On Bowan Downs property, north-east of the Black Mountain, a trachytic basalt outcrops in the valley of a tributary of Paling Yards Creek. It appears to be overlain by a porphyritic trachyte, in which beds of trachyte breccia and diatomaceous earth occur. The phenocrysts are of glassy orthoclase, and the colour of these rocks varies from purple-brown to greenish grey. A dark,

resinous, olivine trachybasalt overlies the porphyritic trachytes near "Bowen Downs".

East of Canomodine Creek, too, porphyritic trachytes seem to overlie a basalt which is different to those making up the extensive flows of the Cudal and Toogong districts.

Fine-grained ægirine-trachytes are well developed east of the Black Mountain along the Cargo-Orange road. They have a dark blue-grey colour and resinous lustre when fresh, but readily alter to a grey or yellowish-brown, friable rock. Their stratigraphical position is uncertain, but they appear to be equivalent to the porphyritic trachytes.

The basalts of the Cudal and Toogong districts are probably the youngest of the Tertiary flows. They outcrop north of Cargo along Warree Creek and near Bowen Park; and also along Gerybong, Oaky, Boree and Mandagery Creeks to the west.

The most common type is a dark, fine-grained rock with phenocrysts of glassy plagioclase which are often stained red by hæmatite. In places, the surface of the flow is vesicular and the vesicles are sometimes partly filled with chlorite, calcite or zeolites. At several localities there is evidence of two flows. One mile north of Cudal* the lower flow, a non-porphyritic basalt, rests on a grey decomposed rock, possibly a trachyte tuff. The upper flow is a basalt porphyritic in white plagioclase.

A generalized sequence of the Tertiary lavas, then, is probably as follows:

4. Basalts of the Cudal and Toogong districts.
3. Olivine trachybasalt (localized).
2. Porphyritic and fine-grained trachytes.
1. Fine-grained trachytic basalt.

Pre-basaltic sands and gravels, now quartzites and silicified conglomerates ("grey billy"), are found under and along the margins of the lavas. They also occur in isolated outcrops some distance away from the nearest basalt, indicating the original extent of the latter.

Near "Mandagery", beside Mandagery Creek, silicified conglomerate and sandstone form a large, rounded outcrop more than 30 feet high. Smaller patches of "grey billy" and gravels occur at intervals along Boree and Mandagery Creeks as far as Long's Corner, and thence along the road to Burdett for about two miles.

Other sediments of doubtful age (but lying within the range of Tertiary to Recent) may be noted here.

At several localities (viz. in Barragan and Cargo Gullies, near "Eurella", and in portion 18, Parish of Canomodine), finely-banded, orange-coloured clays occur, and in all except the last-named place they appear to underlie basalt. The clays are soft and sectile, however, and show no hardening or silicification.

White, friable sandstone occurs near the boundary of the Tertiary basalt west of Boree Creek and north of Barragan. Its relation to the basalt is uncertain, but it is probably of Tertiary age. Rocks of similar age and small extent include ferruginous sandstone and hæmatite north of Toogong and between Toogong and Barragan.

Although the sediments of the Gum Flat lead have been referred to a post-Tertiary age (Andrews and Morrison, 1915), it is possible that the lower sediments may be of late Tertiary age, as the time necessary for the accumulation of 370 feet of sediments, and later degradation of the alluvium to form a broad valley, must be considerable.

* Information from bore cores.

No opportunity now exists to examine the sub-surface sediments but according to Andrews and Morrison they consist of "buried river wash and carbonaceous sediments with leaf imprints . . . Superimposed on these are great thicknesses of ferruginous sandy clays flanking an irregular but steeply pitching mass of coarse wash lying against the now-buried valley wall."

(6) *Quaternary*.

Deposits of this age are mainly gravels, ferruginous grit and more recent alluvium.

Characteristic of the limestone country are irregularly distributed areas of gravels, often firmly cemented by hæmatite and limonite. The gravels are best developed south of Cargo, where the limestone deposits are largest. The rounded pebbles are of quartz, quartzite and andesite, indicating that their source was some distance to the east.

The occurrence of these deposits overlying or near the margin of limestones, and their rare association with other rocks, suggests that channels were eroded in the limestone, and that iron-bearing solutions derived from the limestone cemented the gravels, lessening their ability to be transported, so that they remained in the position in which they were cemented.

Deposits of river gravels of post-basalt age occur between the Manildra-Toogong road and Mandagery Creek, and on the north side of Boree Creek, near Toogong. The latter deposit is up to 40 feet thick, and is related to the present course of Boree Creek. The original (pre-basalt) course of the creek is a short distance to the north of the present stream.

Most of the gravel deposits of Canomodine Creek are small, and occur up to 15 feet above the stream. A much higher deposit of gravels, on the north-eastern margin of the Cargo Creek limestone, has already been referred to in the Physiography section.

River and creek alluvium is well developed along the banks of the major streams and near the present source of Cargo Creek. Many of the smaller gullies show thicknesses of up to 30 feet of conglomerates, gravels, sands and clays.

(IV) STRUCTURAL GEOLOGY.

(a) *Folding*.

(i) *Ordovician*. The structure of the Ordovician rocks cannot be determined with certainty, because of the limited exposures. The strike, however, varies from meridional to east-north-east, so that there is probably an unconformity with the overlying Silurian rocks, similar to that recorded near Parkes (Andrews, 1910).

(ii) *Silurian*. The Silurian rocks are folded into a series of anticlines and synclines, with trend varying from north 12° east near Cudal to north 40° west south of Cargo. Both anticlines and synclines plunge either to the north or south, forming elongated domes and basins.

Between the Upper Devonian belts of the Nangar and Columbine Mountains, at least two major anticlines and two major synclines are present in the Silurian rocks; the distance between successive crests or troughs of folds being about five miles.

The folds are somewhat asymmetrical, with steeper dips on the eastern sides of anticlines. The angles of dip vary greatly, but are mostly between 25° and 60°. In general, the angles are greater in the Cargo district, for folding is closer there, and the area is heavily faulted.

The two major anticlines will be referred to as the Cudal-Barragan and Cargo anticlines; these are separated by the Avenel syncline, and another syncline occurs east of Cargo.

The Cudal-Barragan anticline corresponds north of Cudal with the fold figured by Joplin and Culey (page 269, 1937). The trend one mile west of Cudal (where the oldest beds exposed are limestone and clayshales) is north 12° east. The fold continues to the south for $3\frac{1}{2}$ miles until it is intersected by the Oak Creek fault, where the axis is displaced half-a-mile to the west, and the strike changes abruptly to north 28° west. With this strike the fold continues in a southerly direction towards Barragan, where the strike changes to nearer meridional again. South of Barragan, the anticline plunges to the south, and the andesites (occupying the core of the anticline) disappear beneath the surface, giving place to the overlying tuffs.

On the western side of this anticline, successive beds dip to the west at angles between 25° and 50° , as far as Mandagery Creek, where the slates are highly cleaved, and appear to have steep angles of dip. The strike is not constant in the beds west of the anticlinal axis, varying from north 20° west to north 36° east. Minor drag folds occur in the clayshales.

The Avenel syncline north of Avenel is parallel to the Cudal-Barragan anticline, but to the south, where the Canomodine limestone begins to thicken, the strike changes from north 15° west to north 40° west. A minor anticlinal fold appears in the centre of the limestone belt, forming a dome-like structure.

In the vicinity of Gerybong Creek the strata are much disturbed due to the intrusion of a sill, which has lifted the surrounding rocks a distance of about 100 feet.

Folding in the Cargo Andesitic Series. Near Cargo the folding is closer and more complex, and approximates to an anticlinorium. North of Cargo, only isolated data on the strike and dip can be obtained, but in the highly dissected country to the south-east outcrops are better, and reliable information regarding structure may be ascertained from beds of stratified cherts and tuffs in the Andesitic Series.

The variation in strike and dip is shown in Fig. 1. It will be seen that at least three anticlines and two synclines occur across the width of outcrop of the Andesitic Series. The folds plunge to the south-east, and near the headwaters of Spring Creek the variation in strike indicates a steep angle of pitch. The most south-easterly of these folds (a plunging anticline) accounts for the curvature in the outcrop of the Cargo Creek limestone on the south side of Canomodine Creek.

The strike of the fold axes near Cargo varies from north 35° west to nearly north-south further east. On the eastern margin of the Andesitic Series the equivalent of the Cargo Creek limestone occurs in two plunging synclines. North of Canomodine Creek the fold plunges north; south of the creek it plunges south, but only the western side is preserved, as the eastern side has been cut off by a fault.

Between the south-eastern extremity of the Cargo Creek limestone and the Upper Devonian quartzites the strike of the fold axes is nearly north-south; except near the fault junction between andesites and limestone, where the strata curve around in a westerly direction.

(iii) *Upper Devonian and Lower Carboniferous.* Silurian and Upper Devonian rocks are separated by fault junctions in every part of the district except at the south-east corner, where good evidence exists of their mutual structural relations.

There, on the Belubula River, Upper Devonian quartzites striking 350° and dipping west at 17° overlie Silurian tuffs and slates with strike 10° , dipping west at 40° . An unconformity therefore exists, although in many places the trends of Silurian and Upper Devonian rocks are approximately parallel.

The Mandagery Range quartzites dip west along their eastern boundary, but south of Meranburn the strike changes from north-south to north-west

south-east, indicating that the structure may be a large plunging syncline or basin.

On the eastern side of the district the structure in the Upper Devonian is again a syncline, with a dome developed on the western side of the fold.

Columbine Mountain is formed of quartzites occupying the central part of the dome, the axis of which has a north-south strike. Canomodine Creek exposes a section through the southern end of this dome, and the strike and dip varies gradually over a distance of half a mile.

The syncline is very asymmetrical, with a steeper western side. On the eastern side conglomerates form a gentle dip slope extending from the foothills of the Black Rock Range almost as far as Columbine Mountain. The structure becomes more complex to the south near Four Mile Creek, where a minor anticline and syncline appear, and outcrops are repeated by faulting.

Only the tuffs and mudstones are of definite Carboniferous age, and these appear to overlie the Upper Devonian rocks conformably.

At the Black Mountain, the structure in the Upper Devonian appears to be a plunging anticline or elongated dome. The western side has been cut off by a major fault, leaving a J-shaped outcrop of the Upper Series (mainly quartzites). Creeks cutting through the quartzites expose good sections. Angles of dip greater than 60° are frequent, and some overfolding has taken place. Shear zones in shaley sandstones have also been noted here.

(b) *Faulting.*

The Columbine Mountain Faults. An important fault zone along the western side of Columbine Mountain and the Black Mountain marks the junction between Silurian and Upper Devonian rocks, and in some places Ordovician strata appear in the faulted area.

The main line of faulting has a general north-south trend and has been traced north as far as Paling Yard Creek and south to the Belubula River. From reconnaissance work further south there is reason to believe that the fault continues towards Woodstock.

Evidence of the fault may be seen at several places, particularly at Regan's Creek (three miles south-east of Cargo) and on Paling Yards Creek.

On Regan's Creek, about 200 yards north of the Canangles Road, Upper Devonian quartzites, shales and mudstones outcrop along the creek bed, striking 12° and dipping westerly at 48° . On the west bank of the creek, 120 feet vertically above it, is the junction between Upper Devonian (or Lower Carboniferous?) conglomerate and Silurian tuffs of the Andesitic Series, which underlie the equivalent of the Cargo Creek limestone. The limestone has a strike of 10° and dips west at $25-30^\circ$, so that it appears to overlie the Upper Devonian rocks.

A little further north, Ordovician slates appear at the boundary of the Upper Devonian strata. They are bounded to the west by a fault parallel to the main fault, and they adjoin a limestone which is at the top of the Andesitic Series, so that a considerable thickness of the Silurian is missing. Furthermore, a rapid thinning-out cannot be assumed, for the full sequence of the Andesitic Series occurs on the south side of the syncline.

Still further north the main limestone belt adjoins the Upper Devonian series, and because of an oblique thrust fault Ordovician cherts and slates appear once again on the west side of the major fault. Another oblique fault to the north brings the Andesitic Series against the Ordovician and Upper Devonian rocks (Fig. 2).

The evidence of the same major fault is equally strong on Paling Yard Creek, where shales of the Lower Series of the Upper Devonian appear to dip beneath

the equivalent of the Cargo Creek limestone. The limestone occurs in a narrow plunging syncline, and overlies (on the west side of the fault) a great thickness of the Andesitic Series.

Canangle Creek exposes a section through the quartzites which shows a gradual overturning of the strata as the fault is approached. This, together with the exposure of the actual fault plane in Regan's Creek, indicates that the major fault is a high angle thrust; Silurian rocks have been thrust over Upper Devonian and the downthrow side is the eastern side.

It is difficult to classify the other faults in the Regan's Creek area, but it is likely that normal and thrust faults alternate to produce the alternate strips of Silurian and Ordovician rocks. The most north-westerly of these oblique faults cuts off the limestone in the plunging syncline, then turns south through the Andesitic Series, where it is difficult to trace. It may join with the fault

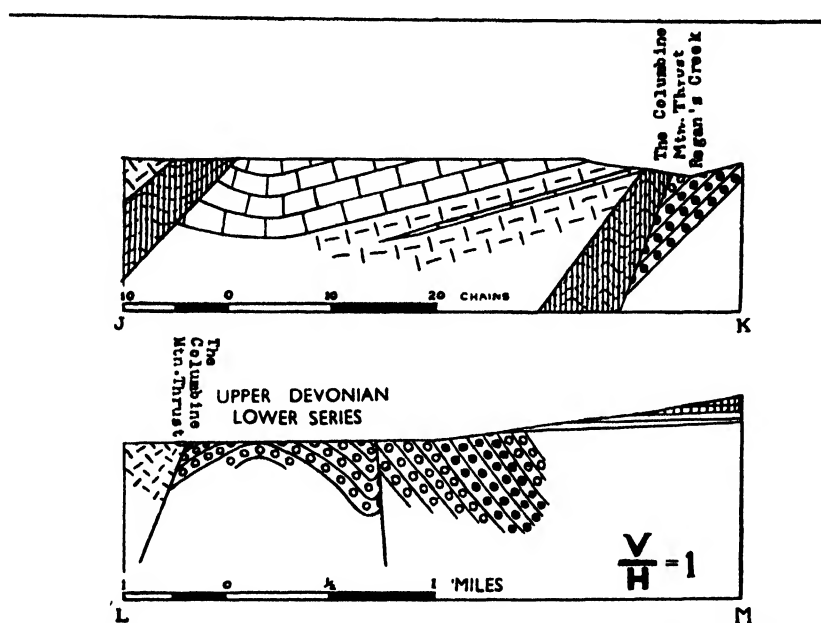


Fig. 2.—Sections across the Columbine Mountain Thrust.

which terminates the south-eastern extent of the Cargo Creek limestone, but with this fault the upthrow side is to the east, not the west (see Fig. 1). The last-named fault turns south-east, cutting off the southern extent of the Andesitic Series, and ultimately joining the Columbine Mountain thrust near the Belubula River.

An oblique fault five miles south-east of Cargo displaces both the faults just described. It strikes west 25° north, and offsets the Silurian-Upper Devonian boundary about 20 chains. The Cargo Creek limestone is also cut off by this fault.

On the eastern side of Columbine Mountain the angle of dip of the quartzites changes abruptly from a low angle to 65° (easterly) and successive strata are red shales, then conglomerates. It is likely that a bedding plane fault is present, dipping east.

The Canomodine Faults. Several faults occur near Canomodine Station, and some displace the boundary of the Canomodine limestone with the underlying beds.

The largest of these follows the course of Canomodine Creek for a short distance, and the actual fault junction may be seen on the west bank of Canomodine Creek downstream from the bridge, and on Back Creek near Canomodine

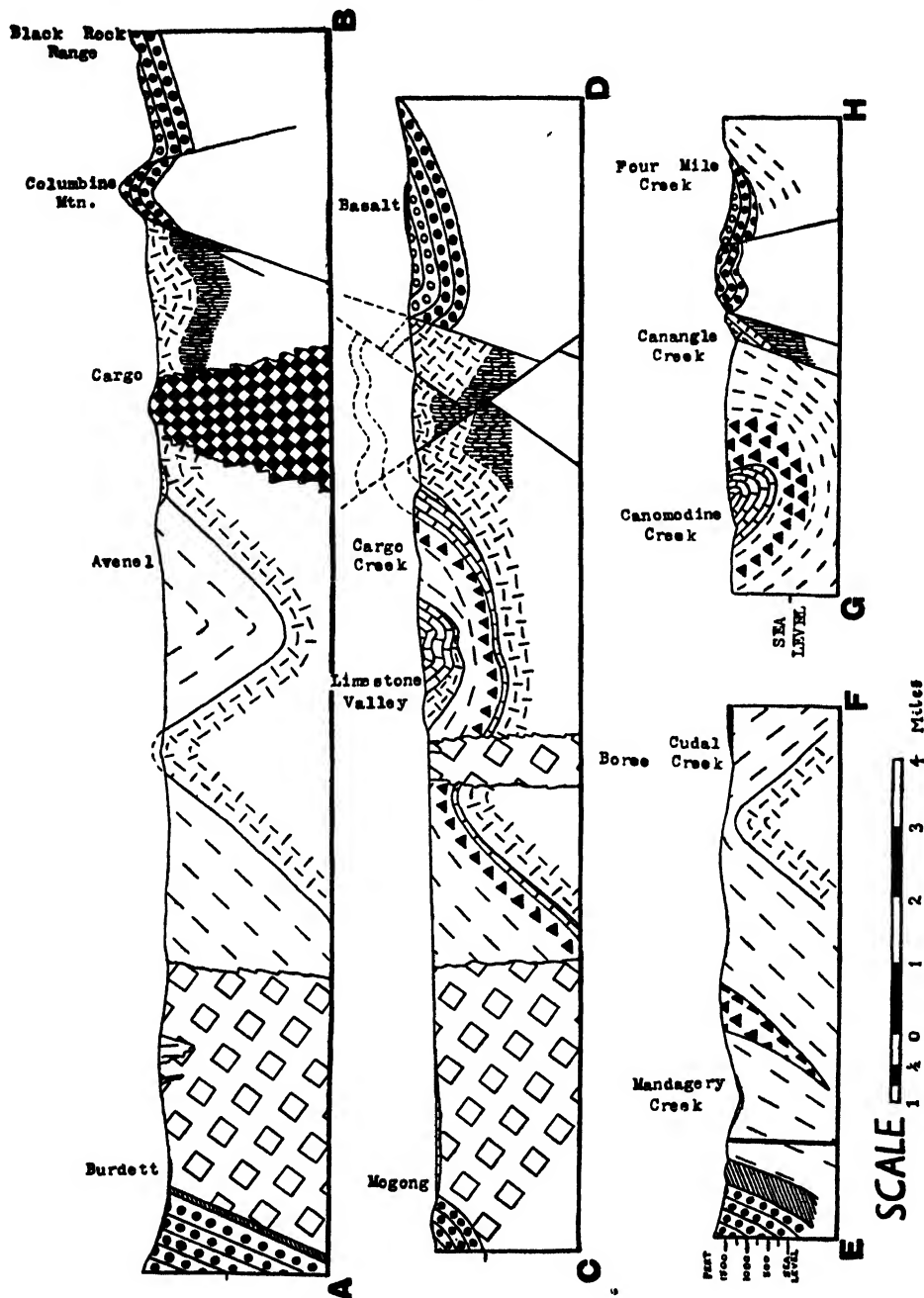


Fig. 3.

Station. The strike is approximately west-south-west, and the south-east side is the downthrow side.

A smaller fault crosses the road one mile west of Canomodine. It has a strike of south 25° west, and displaces limestone and tuff beds about 400 yards.

Two other small faults affect the junction between the Canomodine limestone and the tuffs near the Cargo-Canowindra road.

The Oaky Creek Fault. In this case the fault plane is covered by alluvium and Tertiary basalt. The fault seems to trend east 30° north along Oaky Creek, thence in an east-west direction along Boree Creek.

The evidence for the presence of a fault along this line depends mainly on the sudden disappearance of the Andesitic Series and the displacement of the axis of the Cudal-Barragan anticline.

The axis, which, south of Oaky Creek, may reasonably be suspected to lie near the centre of the Andesitic Series, is displaced about three-quarters of a mile in a north-east direction north of Oaky Creek. Here, thin tuff beds occur in the core of the fold, these being at a higher horizon than the andesites. The downthrow side of the fault is to the north, as the southern side has been eroded to expose older beds. The abrupt change in strike is probably due to a horizontal movement of one block relative to the other, coupled with a slight rotary movement. A horizontal movement is postulated because no appreciable displacement of the anticlinal axis is to be expected, as the fault is approximately a dip fault. Alternatively, the horizontal displacement may be due to a westerly sloping axial plane.

The Shear Zone West of Mandagery Creek. A north-south zone of shearing exists in the uppermost Silurian sediments on the west side of Mandagery Creek. Slates have been converted to phyllitic rocks, and small intrusions of porphyry have suffered shearing. All the rocks in this zone show evidence of the introduction of solutions containing iron and silica; the slates, and even the rhyolites, are jasperized in places, and quartz veins penetrate the Upper Devonian quartzites. The latter have steep dips, and sometimes show overfolding. The Lower Series of the Upper Devonian is missing along this line, probably due to faulting.

Numerous minor faults have been found throughout the district, but only two of these appear on the map (Plate XXI). These displace limestone beds south of the Cudal-Manildra road.

The Age of the Faults. Both the Columbine Mountain fault and the Mandagery shear zone are post-Upper Devonian, pre-Tertiary. As Lower Carboniferous strata are conformable with the Upper Devonian, the diastrophic epoch to which these faults belong must be placed between the close of Lower Carboniferous and the Tertiary period. The folding of the Upper Devonian rocks must also have taken place within this period.

The age of most of the other faults in the area is uncertain, and it is possible that some may have occurred between the end of the Silurian and the beginning of the Upper Devonian (e.g. the Oaky Creek fault).

Jointing. The directions of jointing vary greatly, as the trends of the folds vary, and local folding and faulting complicate the patterns. Near Cargo the dominant jointing is east-west and north-east south-west in the Andesitic Series, and igneous dykes to the north follow these directions.

V. INTRUSIVE ROCKS.

Nearly all the intrusive rocks of the district invade Silurian strata, and so far none has been found invading Upper Devonian rocks. The age of the intrusives seems to be within the period between the close of the Silurian and the beginning of the Upper Devonian; probably late Middle Devonian.

(1) *Quartz Porphyries and Granite Porphyry.*

Near Dulladerry Creek two acid dykes invade the Upper Silurian slates. They are both composed of a pale grey felsitic rock, with small phenocrysts of

quartz and felspar, and resemble the more leucocratic of the rhyolites. It is possible that they were feeders to these flows, and are of late Silurian age.

The intrusion at Cargo is in the form of a small boss of acid hypabyssal types. It has been suggested that the rocks may be a pre-Silurian inlier (Andrews and Morrison, 1915), but definite intrusive relations with the Andesitic Series have been found in several gullies near the Cargo-Canowindra road.

At least two main types of rock are present; one a quartz porphyry, with or without felspar phenocrysts, the other a felsite, with a few small phenocrysts of acid plagioclase. The quartz porphyries contain phenocrysts of idiomorphic quartz and felspar in a cream or grey aphanitic groundmass. Pyrites is usually present, and may replace the altered felspar. The felsites are of the same colour, but do not show quartz phenocrysts. The intrusion is tentatively assigned a late Silurian age, because of its affinities with the acid dykes of Dulladerry Creek.

On the Cudal-Manildra road $3\frac{1}{2}$ miles north-west of Cudal, a small boss of quartz felspar porphyry invades the Silurian clayslates. Phenocrysts of white, albitized felspar, pink orthoclase and brown vitreous quartz are set in a dark grey stony groundmass. Some varieties resemble the Manildra granite porphyry, and it is considered that the intrusion is a phase of this rock type.

The typical granite porphyry of Manildra has been found at only one place in this district, viz. four miles north-east of Toogong. The rock contains large idiomorphic phenocrysts of quartz, pink felspars and chloritized biotite, in a pink, fine-grained to aphanitic groundmass.

An intrusive mass of quartz keratophyre invades the Silurian slates north of Sterling Public School. The intrusion is in the form of a sill, for both overlying and underlying clayslates have been converted to hornfelses. The base of the sill is at the level of Gerybong Creek, and the igneous rock forms a cliff about 100 feet high, capped by silicified sediments.

In most places the rock is very fine-grained, resembling the felsite of the Cargo intrusion. Thin sections show small phenocrysts of albite, quartz and orthoclase in a cryptocrystalline, partly glassy groundmass.

(2) *Granophyres and Porphyrites.*

Acid hypabyssal rocks ranging from microgranite to augite-rich granophyre occur in a discontinuous dyke extending from Mandagery Creek north of Toogong to a point $1\frac{1}{2}$ miles north-east of Cargo.

The strike varies from north 40° west at "Derowie" to east-west near Cargo. Only isolated lenticular outcrops occur, and the maximum width of the intrusion is eight chains. North-east of Cargo the dyke is intersected by a dyke of monzonite porphyry striking north 48° east. The dykes have been injected along dominant joint planes in the country rock.

The typical granophyre is a pink rock with small phenocrysts of sericitized plagioclase in a fine-grained granophyric groundmass containing orthoclase, quartz, biotite, and sometimes augite. A related rock type, an augite porphyrite from west of Sterling Public School, probably belongs to the same dyke. It has been intersected by a later dyke of porphyritic dolerite. Granophyres have also been found near Bowan Park, and north-east of Canomodine.

The monzonite porphyry has large phenocrysts of pale green chloritized plagioclase and prismatic augite in a fine-grained pink groundmass of plagioclase, augite and orthoclase. A similar rock occurs at the margin of the granophyre in some parts of the east-west dyke, and is of a slightly earlier age. The porphyrite which invades Ordovician slates in Regan's Creek (east of Cargo) is related to these rocks.

All these hypabyssal types have been subjected to intense deuteritic alteration, with the production of chlorite, sericite, kaolin, albite, epidote and prehnite.

(3) *The Garnetiferous Porphyry.*

A quartz felspar porphyry with sparsely distributed red garnet occupies large areas south of Toogong. It also occurs between Meranburn and Toogong, and south of Cargo.

In hand specimen the rock is of a medium grey colour, with phenocrysts of white felspar, colourless quartz and chloritized biotite or hornblende.

Similar rocks from the Wellington district have been described as garnetiferous tuffs (Basnett and Colditz, 1945). However, the rocks show intrusive relations in the Cargo district, and there is some evidence for regarding them as intrusive porphyries. They are equivalent to the so-called "intrusive tuffs", which are a feature of the Silurian igneous activity in other parts of New South Wales (Browne, 1929).

(4) *Dolerites.*

Doleritic intrusions occur throughout the district in dykes and small bosses. Except for the porphyritic dolerite previously noted, the dyke rocks are fresh, ophitic types, whereas the dolerites of the bosses have suffered much deuteritic alteration.

The porphyritic dolerite occurs in a north-south trending intrusion west of Sterling Public School. The rock has phenocrysts of plagioclase and augite in a fine-grained, grey, doleritic groundmass.

Small bosses of dolerite occur north-west of Cudal and on Canomodine Creek, south-east of Cargo. They are medium-grained rocks consisting of pyroxene, plagioclase and a little apatite and sphene, with deuteritic minerals chlorite, calcite and epidote. Magnetite or ilmenite is usually present, and some quartz is usually set free by deuteritic activity.

The dolerites occurring in dykes are mostly very similar, fine to medium-grained types consisting mainly of plagioclase and augite in ophitic or sub-ophitic relationship. A rock from a dyke on Mandagery Creek (west of Cudal) has small amygdules of calcite and chlorite, while another to the south contains quartz and micropegmatite, with ilmenite, sphene and apatite.

A most unusual dyke rock from Canangle Creek shows large phenocrysts of hornblende, and occasionally plagioclase. It varies from a hornblende porphyrite to a hornblende lamprophyre, according to the percentage of plagioclase present as phenocrysts.

VI. SUMMARY.

Most of the stratified rocks of the Cargo-Toogong district are of Silurian and Upper Devonian age. They have been folded into plunging anticlines and synclines, which, when a large area is considered, show themselves to be greatly elongated domes and basins. A great deal of faulting has taken place, especially along the boundaries of Silurian and Upper Devonian rocks.

Points of some structural and stratigraphical significance are: (1) the unconformity between Silurian and Upper Devonian rocks; (2) the discovery of Lower Carboniferous strata and their apparent conformity with the Upper Devonian.

Numerous minor intrusions invade the Silurian rocks, and these have been briefly noted. A peculiar garnet-bearing rock, previously described as a tuff further north, seems to show intrusive relations.

Tertiary lavas partly cover the older rocks, and have flowed down old river valleys from the direction of Mt. Canobolas. The chief types are basalts, but trachytes become more abundant closer to the volcanic foci.

VII. ACKNOWLEDGEMENTS.

I wish to acknowledge the help and advice given by Dr. G. A. Joplin, who introduced me to this interesting area, and I am also indebted to other members of the staff of the Geology Department of the University of Sydney and to Dr. A. B. Walkom and Mrs. K. Sherrard.

For hospitality during field work, my thanks are due to Mr. and Mrs. V. T. O'Connell and Mrs. C. Wythes and family, of Cargo; and to Mr. and Mrs. H. J. Balcomb and family and Mr. and Mrs. N. H. Balcomb of Toogong.

During the field work, I was accompanied on one occasion by Mr. G. M. Dimmock, and on another occasion by Messrs. T. G. Vallance and K. R. Sharp.

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EXPLANATION OF PLATE XXI.

Geological Map of the Cargo-Toogong District.

Note.—The minor intrusions are lettered g, p, pr and d, denoting rock types related to granophyre, porphyry, porphyrite and dolerite respectively.

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

April 7th, 1948.

The Annual Meeting, being the six hundred and forty-eighth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The Acting-President, Dr. F. Lions, was in the chair. Eighty-five members and visitors, including the senior Trade Commissioner for Canada, Mr. C. W. Croft, were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

R. L. ASTON, B.Sc., B.E. (*Syd.*), M.Sc., Ph.D. (*Camb.*), A.M.I.E. (*Aust.*).

Vice-Presidents :

J. A. DULHUNTY, D.Sc.
F. LIONS, B.Sc., Ph.D., A.R.I.C.

D. P. MELLOR, D.Sc., F.A.C.I.
F. R. MORRISON, A.A.C.I., F.C.S.

Hon. Secretaries :

O. U. VONWILLER, B.Sc., F.Inst.P.

H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

Hon. Treasurer :

A. BOLLIGER, Ph.D., F.A.C.I.

Members of Council :

R. C. L. BOSWORTH, M.Sc., D.Sc. (*Adel.*),
Ph.D. (*Camb.*), F.A.C.I.
IDA A. BROWN, D.Sc.
R. O. CHALMERS, A.S.T.C.
F. P. J. DWYER, D.Sc.
H. O. FLETCHER.
F. N. HANLON, B.Sc.

C. J. MAGEE, D.Sc.Agr. (*Syd.*),
M.Sc. (*Wis.*).
C. ST. J. MULHOLLAND, B.Sc.
D. J. K. O'CONNELL, S.J., M.Sc.,
F.R.A.S.
W. B. SMITH-WHITE, M.A. (*Cantab.*),
B.Sc. (*Syd.*).

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and, on the recommendation of Dr. G. D. Osborne, seconded by Mr. J. Wallis Powell, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 29th FEBRUARY, 1948.

LIABILITIES.

1947.		1947.			
£		£	s.	d.	
92	Accrued Expenses	188	7	8	
15	Subscriptions Paid in Advance	25	4	0	
60	Life Members' Subscriptions—Amount carried forward	102	0	0	
—	James Cook and Edgeworth David Medals—Amount carried forward	200	0	0	
	Trust and Research Funds (detailed below)—				
	Clarke Memorial	1,928	3	8	
	Walter Burfitt Prize	1,097	7	10	
	Liversidge Bequest	725	15	0	
	Monograph Capital Fund	3,421	13	4	
6,996		7,172	19	10	
25,979	ACCUMULATED FUNDS	25,877	0	11	
	Contingent Liability—In connection with perpetual leases granted to Australian National Research Council and the Pharmaceutical Society of N.S.W.—				
(902)	Maximum Liability £901 16s. 8d.				
<u>£33,142</u>		<u>£33,565</u>	<u>12</u>	<u>5</u>	

ASSETS.

1947.		1947.			
£		£	s.	d.	
293	Cash at Bank and in Hand	595	17	10	
	Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value—				
	Held for—				
	Clarke Memorial Fund	1,800	0	0	
	Walter Burfitt Prize Fund	1,000	0	0	
	Liversidge Bequest	700	0	0	
	Research Fund	3,000	0	0	
	General Purposes	4,360	0	0	
10,860		10,860	0	0	
61	Prepayment	160	10	6	
	Debtors for Subscriptions	117	12	0	
	Deduct Reserve for Bad Debts	117	12	0	
14,715	Science House—One-third Capital Cost	14,715	0	0	
6,800	Library—At Valuation	6,800	0	0	
373	Furniture—At Cost—less Depreciation	396	10	1	
30	Pictures—At Cost—less Depreciation	28	14	0	
10	Lantern—At Cost—less Depreciation	9	0	0	
<u>£33,142</u>		<u>£33,565</u>	<u>12</u>	<u>5</u>	

TRUST AND MONOGRAPH CAPITAL FUNDS.

	Clarke Memorial.			Walter Burfitt Prize.			Liversidge Bequest.			Monograph Capital Fund.		
	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
Capital at 28th February, 1947 ..	1,800	0	0	1,000	0	0	700	0	0	3,000	0	0
Revenue—												
Balance at 28th February, 1947	108	13	8	65	7	10	—			322	8	4
Interest for twelve months ..	64	13	9	34	15	0	25	15	0	99	5	0
	173	7	5	100	2	10	25	15	0	421	13	4
Deduct Expenditure ..	45	3	9	2	15	0	—			—		
Balance at 29th February, 1948 ..	£128	3	8	£97	7	10	£25	15	0	£421	13	4

ACCUMULATED FUNDS.

	£	s.	d.
Balance at 28th February, 1947	25,978	10	3
Less—			
Deficit for twelve months (as shown by Income and Expenditure Ac- count)	£81	11	4
Increase in Reserve for Bad Debts	19	18	0
	101	9	4
	£25,877	0	11

G. D. OSBORNE,
Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of the Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 29th February, 1948, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 24th March, 1948.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1947, to 29th February, 1948.

1946-7.		1947-8.	
£		£	s. d.
355	To Printing and Binding Journal—Vol. 80	506	19 0
363	„ Salaries	361	10 0
125	„ Library—Purchases and Binding	150	4 4
68	„ Printing—General	89	17 4
103	„ Miscellaneous	127	8 2
95	„ Postage and Telegrams	95	0 8
43	„ Rent—Science House Management Committee ..	45	15 11
40	„ Cleaning	37	0 0
22	„ Depreciation	23	7 0
19	„ Telephone	18	19 10
15	„ Insurance	15	3 7
13	„ Audit	18	18 0
8	„ Electricity	11	19 11
—	„ Repairs	17	18 0
	„ Reprints—		
	Expenditure £205 13 3		
	Less Received 89 12 11		
		116	0 4
	„ Annual Dinner—		
	Expenditure £69 8 7		
	Less Received 48 15 0		
		20	13 7
	„ Conversazione—Atomic Education—		
	Expenditure £39 4 0		
	Less Received 8 0 0		
		31	4 0
1,269		1,687	19 8
255	„ Surplus for Twelve Months		
£1,524		£1,687	19 8

1946-7.		1947-8.	
£		£	s. d.
522	By Membership Subscriptions	556	10 0
400	„ Government Subsidy	400	0 0
436	„ Science House—Share of Surplus	482	10 0
145	„ Interest on General Investments	156	18 4
6	„ Receipts from Reprints	—	
1	„ Other Receipts	—	
8	„ Proportion of Life Members' Subscriptions ..	10	10 0
6	„ Annual Dinner	—	
		1,606	8 4
—	„ Deficit for Twelve Months	81	11 4
£1,524		£1,687	19 8

The Annual Report of the Council (1947-48) was read, and on the motion of Dr. F. P. J. Dwyer, seconded by Mr. A. S. Le Souef, adopted.

REPORT OF THE COUNCIL, 1947-48 (RULE XXVI).

By resignation the Society has lost six members: Joan Marian Beattie, Reginald Frank Cane, Norman Augustus Faull, Jack Campbell Norrie, Douglas Elwood White and Guy Carrington Yates.

The membership now stands at 332, 25 new members having been elected during the year namely Peter Beckmann, Gregory Stewart Buchanan, Gladys Olive Curry, Alan Marchant Downes, Naida Sugden Gill, Stuart Frederick Gill, Neil Ernest Goldsworthy, Lennard Robert Hall, Justin Ernst Humpoletz, Raymond James Wood Le Fevre, James Charles Lloyd, Patrick Reginald McMahon, Charles Joseph Magee, Leo Edmund Maley, George E. Mapstone, Peter Nordon, Adrian Noel Old, Nancy Evelyn Ray, Reginald John Ray, Fritz Henry Reuter, Arthur Sinclair Ritchie, Bruce Ritchie, William Broderick Smith-White, Gordon Keyes Webb and Ronald Louis Werner.

Eleven ordinary meetings of the Council and one special meeting were held during the year commencing 1st April, 1947, at which the average attendance was 14. During the same period nine general monthly meetings were held, the average attendance being 35.

The special meeting of the Council was held to discuss arrangements for the *Conversazione* held on the 8th October, 1947, in connection with the Society's campaign on Atomic Education.

Election of Honorary Members.—The following were elected to honorary membership of the Royal Society of New South Wales at the annual and general monthly meeting held on 2nd April, 1947: Sir Harold Spencer Jones, M.A., D.Sc., F.R.S., and Professor F. Wood Jones, D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (London), F.R.S., F.Z.S.

Election of Councillors.—Dr. F. P. J. Dwyer and Mr. W. B. Smith-White were elected to Council at the meeting held on the 27th August, 1947, in place of Mr. R. S. Nyholm and Miss P. Rountree, who had resigned from Council owing to their impending departure overseas.

Addition to Rule V.—The following addition has been made to Rule V (first paragraph): "A copy of the list shall be posted to each financial member of the Society not less than ten days before the closing date for nominations." The addition has been made to ensure that members receive the list of Council's recommendations for office-bearers in ample time to submit further nominations if desired.

Thirty-five papers were accepted for reading and publication during the year, and the following short addresses and lecturettes were given:

"Submarine Canyons with special reference to recent discoveries off the South Australian Coast", by G. D. Osborne, D.Sc. (Syd.), Ph.D. (Camb.).

"Some New American Research Tools", by F. Lions, B.Sc., Ph.D., A.R.I.C.

"Stellar Energy", by Harley Wood, M.Sc., A.Inst.P., F.R.A.S.

"Separation of Isotopes by Gaseous Diffusion", by R. C. L. Bosworth, M.Sc., D.Sc. (Adel.), Ph.D. (Camb.), F.A.C.I., F.Inst.P.

"Radioactive Tracers in Chemistry", by F. Lions, B.Sc., Ph.D., A.R.I.C.

"Palaeontological Work in the U.S.A.", by I. A. Brown, D.Sc.

"Impressions of Chemical Research Activity in Britain", by T. Iredale, D.Sc., F.R.I.C.

Films.—The following sound films were screened at the general meeting held on the 2nd July, 1947:

"The Body Defences against Diseases."

"The Action of the Kidneys."

"Fuels and Heat."

"Light Waves and their Uses."

Exhibit.—At the general meeting held on the 7th May, 1947, an exhibit of "Synthetic Minerals used in Optical and other Scientific Apparatus" was given by F. M. Quodling, B.Sc.

Demonstration.—At the same meeting a demonstration of "Some Photo-chemical Properties of Tungstic Acid" was given by A. Bolliger, Ph.D., F.A.C.I.

Commemoration of Great Scientists.—At the general meeting held on 5th November, 1947, the following addresses were given:

(1) "Torricelli."

"Helmholtz." Enunciation of the Principle of the Conservation of Energy, by Mr. J. B. Thornton.

(2) "Semmelweis." Prevention of Puerperal Fever.

"Simpson." Introduction of Chloroform Anaesthesia, by Dr. K. Brown.

Popular Science Lectures.—Five Popular Science Lectures were delivered during the months of May, June, August, September and October, and were greatly appreciated by the members of the Society and the general public.

May 15th.—"The Hunter River Valley—a Future T.V.A.?" by W. H. Maze, M.Sc.

June 19th.—"Snakes and Snake Venom", by J. R. Kinghorn, C.M.Z.S.

August 21st.—"Measuring the Face of a Continent—the Use of Radar and Photography in Mapping", by R. L. Aston, B.Sc., B.E. (Syd.), M.Sc., Ph.D. (Camb.), A.M.I.E. (Aust.).

September 18th.—"The Colouring Matter of Plants", by R. M. Gascoigne, M.Sc.

October 16th.—"The Story of Goitre", by Hugh R. G. Poate, M.B., Ch.M. (Syd.), F.R.C.S. (Eng.), L.R.C.P. (Lond.), F.R.A.C.S.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1947 was delivered by Professor H. S. Summers, D.Sc., on 17th July, 1947, the title being "The Teachers of Geology in Australian Universities".

Clarke Memorial Medal.—The Clarke Memorial Medal was awarded to Dr. Hubert Lyman Clark, of the Hancock Foundation, University of Southern California, U.S.A., in recognition of his distinguished contributions to natural science, particularly in regard to the elucidation of the Echinodermata of Australia.

Walter Burfitt Prize.—The Walter Burfitt Prize was awarded to Dr. John Conrad Jaeger, of the University of Tasmania, Hobart, for outstanding contributions in the field of Mathematics.

James Cook and Edgeworth David Medals.—Through the generosity of Mr. H. F. Halloran, one of the oldest Life Members of the Society, two medals would be awarded by the Society :

(1) The James Cook Medal for outstanding contributions to Science and Human Welfare in the Southern Hemisphere. The first recipient of the James Cook Medal was Field Marshal the Rt. Hon. J. C. Smuts, P.C., C.H., K.C., D.T.D., LL.D., F.R.S., Chancellor of the University of Capetown and Prime Minister of the Union of South Africa.

(2) The Edgeworth David Medal, which would be awarded for distinguished scientific researches among younger workers.

Government Grant.—A grant of £400 was received from the Government of New South Wales. The Society greatly appreciates the Government's continued interest in its activities.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition.

Printing of Society's Journal.—Owing to increased cost of labour and material, the cost of printing the Society's Journal and Proceedings, as well as reprints of papers, has increased considerably. Previously the cost of the printing of the Journal, inclusive of reprints, was £13 per sixteen pages. Today's cost is £16, exclusive of reprints, per sixteen pages. This shows an increase of 23%, plus the extra charge for reprints.

Annual Dinner.—The Annual Dinner was held on the 1st April, 1948, at the Union Refectory, the University of Sydney. His Excellency the Governor-General and Miss Betty McKell were present, and the Minister for Education, the Honourable R. J. Heffron, represented the Premier and the State Parliament.

A total of 110 members and friends was present.

Science House.—The Royal Society's share of the profits in Science House during the period March 1st, 1947, to February 29th, 1948, was £482 10s., which represents the highest on record.

Science House Management Committee.—The Royal Society has had as its representatives at the meetings of the Management Committee of Science House Mr. H. O. Fletcher and Mr. F. R. Morrison, and as substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

A.N.Z.A.A.S. Conference, Perth, W.A., 20th-27th August, 1947.—Mr. R. M. Gascoigne, Mr. R. S. Nyholm and the Rev. D. J. K. O'Connell were appointed as delegates to represent the Society.

Dr. Edgar Booth.—Dr. Booth, Chairman of the International Wool Secretariat, London, was welcomed in the Society's Reception Room on 16th April, 1947, on the occasion of his visit to Sydney. Dr. Booth referred to work being carried out by the International Wool Secretariat and discussed scientific liaison activities in relation to research and the wool industry.

Professor Raymond Firth.—Professor Firth, the eminent anthropologist, was welcomed in the Society's Reception Room on 22nd March, 1948.

Visit Overseas of the President, Dr. J. A. Dulhunty.—At a special meeting of the Executive Committee held in May, the President was granted leave of absence for the period of his visit abroad to confer with authorities on coal research and the coal industry. The visit was sponsored by the C.S.I.R., the University of Sydney and the B.H.P. Co. Ltd., and arrangements had been made for visits to England, the Continent and the U.S.A. During the President's absence from Sydney, Dr. F. Lions was appointed Acting President of the Society.

Monographs.—At the Council meeting held on the 30th June, 1947, it was decided to publish one or two Monographs per annum, on physical and biological sciences, the funds to be derived from the interest on the present Research Fund. The name of the latter had now been changed to the Monograph Capital Fund.

Payment to Authors.—As the period for payment of five shillings per page to authors had expired as from the 24th July, 1947, it was agreed that the costs of a draughtsman's services would be made available, if required, to authors of papers.

Conversazione.—A very successful conversazione was held on the 8th October, 1947. Following communications from the Association of Scientists for Atomic Education Inc. and the Emergency Committee of Atomic Scientists, headed by Professor Albert Einstein, the Society had decided to open its campaign on atomic education with the conversazione, at which short addresses were given by the Governor of New South Wales, the Chancellor of the University of Sydney, the Minister for Education and the Acting President. Many interesting exhibits were arranged, including a number by courtesy of the heads of departments at the University of Sydney and the C.S.I.R., the Colonial Sugar Refining Co. Ltd., the Sydney Technical College and the Museum of Technology and Applied Science. The Senate of the University of Sydney co-operated by making available the Great Hall for the function, and the Director of the Botanic Gardens assisted with the loan of palms.

The donation of the electrical wiring service to the exhibits by Mr. Churchill, and the services rendered by Mr. Baxter, Yeoman Bedell, and Staff were greatly appreciated.

Sidey Summer-time Medal.—At the request of the President of the Royal Society of New Zealand, the Sidey Summer-time Medal was presented to Dr. D. F. Martyn, of the Mt. Stromlo Observatory, Canberra, at the monthly meeting held on 5th November, 1947. The Medal had been awarded to Dr. Martyn for his work on radar and the receipt of radio waves from the sun.

Meetings of U.N.E.S.C.O., National Co-operating Committee.—Dr. R. L. Aston was chosen to represent the Royal Societies of Australia on the Scientific Co-operating Committee of U.N.E.S.C.O. The meetings, arranged by the Commonwealth Office of Education, were held on the 1st and 2nd March, 1948.

Dr. Aston stressed the need for representation of biological, as well as physical, sciences on the committee.

Collection of Pure Chemical Substances.—At the request of U.N.E.S.C.O., communicated through Professor J. Timmermans, of the University of Brussels, the Society is co-operating with the Australian National Research Council in implementing the proposal to build up a central collection of pure chemicals for the benefit of scientists all over the world.

Government Assistance for Fundamental Research in Australian Universities.—The Society informed the Federal Government that it gave full support to the request of the Australian National Research Council for increased government funds for fundamental research in Australian Universities.

The Library.—The amount of £57 0s. 5d. has been expended on the purchase of periodicals and the amount of £16 10s. spent on repairs to the lighting system; the total sum spent on the Library over the past twelve months is therefore £73 10s. 5d. The binding for 1947-48 is not yet completed owing to lack of suitable cloth, which is imported, and consequently no account has been received from the bookbinders.

Exchanges.—The number of volumes now being sent to other societies is 387.

Accessions.—For the twelve months ending February, 1948, the number of accessions entered in the catalogue was 3,226 parts of periodicals.

Volumes on Loan to the Sydney Technical College Library.—A number of volumes representing incomplete sets were placed on loan to the Sydney Technical College Library for the benefit of Science students.

The loans have been made subject to conditions which will ensure every care being taken of the volumes.

Rationalization of the Libraries of the Linnean Society of New South Wales and the Royal Society of New South Wales.—During the past twelve months the Linnean Society of New South Wales has handed over to the Society's library all volumes requested under the rationalization scheme. On its side, the Royal Society of New South Wales has also given to the Linnean Society of New South Wales those volumes required to complete the Linnean Society's sets under the library rationalization scheme.

Reorganization of Library and Store.—The library and store have been reorganized, and new shelving has been erected for storage of journals for exchange and other publications.

Borrowers and Readers.—Members and visitors reading in the library numbered 17.

The number of books and periodicals borrowed by members, institutions and accredited readers was 285.

Among the institutions which made use of the arrangements for inter-library borrowing were: Food Preservation Laboratories, C.S.I.R., Drug Houses of Australia, Sydney University Medical Library, National Standards Laboratory, C.S.I.R., Fisher Library, C.S.I.R., Canberra, Colonial Sugar Technical Library, Sydney County Council Technical Library, Australian Paper Mills, Department of Public Health, Elliotts and Australian Drugs, Sydney Technical College, Royal Society of Tasmania, New England University College, Pastures Protection Board, McMaster Laboratories, M.W.S. and D. Board, Geology Department, University of Sydney Kraft Cheese, Forestry Department, Serum Laboratories, Melbourne, Melbourne University Library, Australian Glass Manufacturers, By-Products and Chemicals Ltd., Ministry of Post-War Reconstruction and Veterinary Research Station, Glenfield.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected members of the Society: Dorothy Carroll and Ilse Rosenthal-Schneider.

Election of Honorary Members.—The following were elected to honorary membership of the Society: Sir Robert Robinson and Professor Marcus Oliphant.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1948 to Dr. A. B. Walkom.

Walter Burfitt Prize.—The announcement was made of the award of the Walter Burfitt Prize for 1948 to Dr. J. C. Jaeger.

James Cook Medal.—The announcement was made of the first award of the James Cook Medal to Field Marshal the Rt. Hon. J. C. Smuts.

Election of Auditors.—On the motion of Dr. Bosworth, seconded by Mr. Challinor, Messrs. Horley & Horley were re-elected as Auditors to the Society for 1948–1949.

Presidential Address.—As the President was abroad, the Acting President announced that Council had decided to ask the retiring President, Dr. J. A. Dulhunty, to deliver his address when he returned from overseas.

The following papers were read by title only: "A Gens of Dalmanitid Trilobites", by E. D. Gill, B.A., B.D.; "Occultations observed at Sydney Observatory during 1947", by W. H. Robertson, B.Sc.; "A Cell for an 11½-inch Lens", by H. W. Wood, M.Sc.; "Micro-metrical Measures of Double Stars", by H. W. Wood, M.Sc.; "The Paracloacal (Anal) Glands of *Trichosurus vulpecula*", by A. Bolliger, Ph.D., and W. K. Whitten.

Address.—The Acting President welcomed Professor Griffith Taylor, Professor of Geography at the University of Toronto, formerly of Sydney University, who delivered an interesting address on the essential points of nation planning from a geographical, geological and physiographical viewpoint.

Dr. Lions, the Acting President, welcomed the newly elected President, Dr. R. L. Aston to the Presidential chair. Dr. Aston briefly acknowledged the honour.

A vote of thanks to Dr. Lions for his services to the Society as Acting President, in the absence of the President, was proposed by Professor Vonwiller, and was carried by acclamation

F. LIONS,
Acting President.

May 5th, 1948.

The six hundred and forty-ninth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Forty-one members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of seven candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Leslie Arthur Cole, Kenneth George Mosher.

Popular Science Lecture.—It was announced that the first in the series of Popular Science Lectures would be given by Professor N. A. Burges on 20th May, 1948, and would be entitled "The Struggle between Fungi and Roots".

Library.—The following accessions were received: 185 parts of periodicals, one purchase, two books, 27 back numbers.

The following paper was read:

"The Essential Oil of a Physiological Form of *Boronia ledifolia* (Gay)", by A. R. Penfold, F.A.C.I., F.C.S., and F. R. Morrison, A.A.C.I., F.C.S.

Discussion.—The following papers were presented for discussion:

"A Cell for an 11½-inch Lens", by H. W. Wood, M.Sc.

"A Survey of Anthocyanins in the Australian Flora", by R. M. Gascoigne, E. Ritchie and D. E. White.

Exhibit.—"Bouncing Putty", by Dr. D. P. Mellor.

June 2nd, 1948.

The six hundred and fiftieth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Mr. F. R. Morrison, was in the chair. Thirty-seven members and visitors were present. The minutes of the previous meeting were read and confirmed.

The deaths were announced of the following: George Frederick Birks, a member since 1923; Rev. Ernest Norman McKie, a member since 1932.

The certificates of nine candidates for admission as ordinary members of the Society were read for the first time.

The certificates of seven candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Paul Burke Andrews, Alan Victor Jopling, Frank Oswald Kimble, Harry Neil Scott Schafer, Kenneth Raeburn Sharp, Neville Cecil Stevens, Judith Zingel.

Extension Board Lectures.—An announcement was made in connection with the series of Extension Board lectures, the titles and dates as under :

"The Atom and Radioactivity", by Dr. D. P. Mellor, 5th July, 1948.

"Artificial Transformations and Nuclear Fission", by Dr. R. E. B. Makinson, 12th July, 1948.

"Atomic Physics and Human Welfare (Generation of Power : Radioactive Tracers)", by Dr. F. Lions, 19th July, 1948.

"International Control of Atomic Energy", by Dr. G. H. Briggs, 26th July, 1948.

Popular Science Lecture.—It was announced that the second in the series of Popular Science Lectures would be given by Dr. C. J. Magee, on Thursday, 17th June, 1948, and would be entitled "Plant Growth Regulators or Hormones".

It was announced that a preliminary announcement of the Seventh Pacific Science Congress of the Pacific Science Association had been received. The Congress to be held at Auckland and Christchurch, New Zealand, February 2nd to 23rd, 1949.

It was announced that reprints published in the Society's Journal from 1904 to 1930 would be available to members, *gratis*, until the 30th June, 1948.

Library.—The following accessions were received : 273 parts of periodicals, 18 purchases, 62 back numbers.

The following papers were read :

"Spectroscopic Analysis of Alloy Steels", by C. James. (Read by title only.)

"Nitrogen in Oil Shale and Shale Oil. Part I. The Nitrogen Compounds Present in Kerogen", by Geo. E. Mapstone.

"Nitrogen in Oil Shale and Shale Oil. Part II. Organic Nitrogen Compounds in Shale Oil", by Geo. E. Mapstone.

"Nitrogen in Oil Shale and Shale Oil. Part III. Nitrogenous Products from the Pyrolysis of Porphyrins and Proteins", by Geo. E. Mapstone.

"Nitrogen in Oil Shale and Shale Oil. Part IV. Pyrolytic Reactions Involving the Formation and Decomposition of Tar Bases", by Geo. E. Mapstone.

"Electro-Magneto-Ionic Optics", by V. A. Bailey, M.A., D.Phil., F.Inst.P.

Discussion.—The following paper, previously read by title only, was presented for discussion : "The Parafoveal (Anal) Glands of *Trichosurus vulpecula*", by A. Bolliger, Ph.D., F.A.C.I., and W. K. Whitten.

Exhibit.—Enlarged photographs of the Second Positive Spectrum of Nitrogen showing some features of interest, by Professor O. U. Vonwiller and Miss D. P. Tarrant.

July 7th, 1948.

The six hundred and fifty-first General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Fifty-two members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Ernest C. Andrews, a member since 1909 and President in 1921.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of nine candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Eric Harold Boyd, Joan Boyd, Cyril Lloyd Cook, John Cymerman, Oscar Le Maistre Knight, Lawrence Ernest Lyons, Ian Russell Sherwood, Ellice Simmons Swinbourne, Donald Francis Walker.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1948 would be delivered on Thursday, 15th July, 1948, at 8 p.m., by Sir Douglas Mawson, and would be entitled "The Sedimentary Succession of the Bibliando Dome : Record of a Prolonged Proterozoic Ice Age".

It was announced that arrangements had been made to visit the National Standards Laboratory and the Radiophysics Laboratory on the 30th July, at 7.30 p.m., to see some of the things of interest in the laboratories.

It was also announced that in order to give all members opportunity of taking part in the business of Ordinary Monthly Meetings, the Council had decided to introduce some new features, such as Notes and Exhibits, at the meetings.

The Library.—The following accessions were received : 283 parts of periodicals, 20 purchases, 38 back numbers.

The following papers were read :

Presidential Address : "Some New Horizons in Coal Utilisation and Research", by J. A. Dulhunty, D.Sc.

- "Aspects of the Diels-Alder Reaction. Part III. A Note on the Reported Action with Anthraquinone", by R. M. Gascoigne and K. G. O'Brien. (Read by title only.)
- "Contributions to the Study of the Marulan Batholith. Part I. The Contaminated Grano-diorites of South Marulan and Marulan Creek", by G. D. Osborne, D.Sc., Ph.D. (Read by title only.)
- "Nitrogen in Oil Shale and Shale Oil. Part V. The Determination of Nitrogen in Shale Oil and Oil Shale", by Geo. E. Mapstone. (Read by title only.)
- "Nitrogen in Oil Shale and Shale Oil. Part VI. Acid Washing of Crude Shale Oil", by Geo. E. Mapstone. (Read by title only.)
- "Nitrogen in Oil Shale and Shale Oil. Part VII. Distribution of Kerogen Nitrogen on Carbonization", by Geo. E. Mapstone. (Read by title only.)

August 4th, 1948.

The six hundred and fifty-second General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Fifty-five members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Edward M. Wellish, a member since 1920.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Clive Melville Harris, Leo E. Koch, Joan W. Mulley, Betty Yvonne Taylor.

It was announced that the Liversidge Research Lecture would be delivered on Thursday, 19th August, 1948, by Professor Ian Lauder, and would be entitled "Some Recent Work on the Separation and Use of Stable Isotopes".

Request to Authors to Submit Abstracts with Papers.—The Council of the Society suggests to authors that when submitting papers they should give an abstract or summary suitable for publication in the Journal or for transmission to abstracting journals.

The visit to National Standards Laboratory and the Radiophysics Laboratory was reported upon.

The Library.—The following accessions were received: 247 parts of periodicals, 13 purchased parts, 30 back numbers.

The following paper was read:

"The Incomplete Nature of the Symmetry Relations between Thermodynamical Quantities", by R. C. L. Bosworth, D.Sc.

Discussion.—The following paper, previously read by title only, was presented for discussion:

"Contributions to the Study of the Marulan Batholith. Part I. The Contaminated Grano-diorites of South Marulan and Marulan Creek", by G. D. Osborne, D.Sc., Ph.D.

Questions.—The following questions were answered:

"There is evidence that ice ages have occurred simultaneously in both hemispheres of the world—what is the evidence of this?" G. D. Osborne, D.Sc., Ph.D.

"What is a Transcendental Number?" Mr. W. B. Smith-White.

"What are Cosmic Rays?" Dr. R. E. B. Makinson.

September 1st, 1948.

The six hundred and fifty-third General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Thirty-nine members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Eleonara Clara Gyaryas, Julius William Hogarth, Gordon Elliott McInnes, David Stanley Simonett.

Popular Science Lecture.—It was announced that the third in the series of Popular Science Lectures would be given by Mrs. C. Kelly, on Thursday, 16th September, 1948, and would be entitled "The Making of an Australian—A Study in Migration".

The Library.—The following accessions were received: 102 parts of periodicals, 27 purchased parts.

The following papers were read by title only:

"Occurrence of the Brachiopod Genus *Plectodonta* Kozłowski at Bowning, New South Wales", by I. A. Brown, D.Sc.

"Structural Data for the Northern End of the Stroud-Gloucester Trough", by G. D. Osborne, D.Sc., Ph.D., and P. B. Andrews.

"The Concepts of Resistance, Capacitance and Inductance in Thermal Circuits", by R. C. L. Bosworth, D.Sc., Ph.D.

Symposium.—The evening was devoted to a Symposium on "The Education of a Scientist".

The following addresses were given :

"Science in Secondary Education", by Mr. J. B. Thornton.

"The Teaching of Science in the Universities", by Professor N. A. Burges.

"The Scientist and Scientific Method", by Professor K. E. Bullen.

October 6th, 1948.

The six hundred and fifty-fourth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Forty-eight members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of seven candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society : Charles A. M. Gray.

Popular Science Lecture.—It was announced that the fourth in the series of Popular Science Lectures would be given by Mr. N. A. Esserman on Thursday, 21st October, 1948, and would be entitled "Weights and Measures".

The Library.—The following accessions were received : 186 parts of periodicals, 18 purchases, 33 back numbers.

The following paper was read :

"Magnetic Properties of Some Tungsten Bronzes", by P. M. Stubbin and D. P. Mellor, D.Sc.

The following papers were read by title only :

"Coordination Compounds of Copper. Part I. Complex Copper (II) Cuprates (I)", by Clive M. Harris.

"Disproportionation Equilibria in Alkaline Earth Ions", by Noel Hush.

"Geology of the North-Western Coalfield, N.S.W. Part IV. Geology of the Gunnedah-Curlew District", by F. N. Hanlon, B.Sc., Dip.Ed.

"Geology of the North-Western Coalfield, N.S.W. Part V. Geology of the Breeza District", by F. N. Hanlon, B.Sc., Dip.Ed.

"Geology of the North-Western Coalfield, N.S.W. Part VI. Geology of the South-Western Part of County Nandewar", by F. N. Hanlon, B.Sc., Dip.Ed.

Discussion.—The following addresses, delivered at the previous meeting by Mr. J. B. Thornton, Professor N. A. Burges and Professor K. E. Bullen, on "The Education of a Scientist", were presented for discussion :

"Science in Secondary Education",

"The Teaching of Science in the Universities",

"The Scientist and Scientific Method".

After a widely ranging discussion with many participating, Mr. Thornton and Professor Bullen made brief replies.

Questions.—The following questions were answered :

"Why are there black and white races?" Professor A. P. Elkin.

"Why does the moon always turn the same face towards the earth?" Mr. Harley Wood.

November 3rd, 1948.

The six hundred and fifty-fifth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. R. L. Aston, was in the chair. Forty-one members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of seven candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Fred Roy Blanks, Shirley Kathleen Doyle, Bruce Thomas Dunlop, Edward Carson Gardiner, Kenneth Roderick Glasson, Jean Northcott, Hubert Roy Perry.

Nuffield Foundation Dominion Travelling Fellowships.—It was announced advice had been received regarding the Nuffield Foundation Dominion Travelling Fellowships. The awards available would be as follows:

- Three Fellowships in Medicine.
- Two Fellowships in the Natural Sciences.
- One Fellowship in the Humanities.
- One Fellowship in the Social Sciences.

The Library.—The following accessions were received: 104 parts of periodicals, nine purchases.

The following papers were read by title only:

- "Synthesis of Dithiohexestrol Dimethyl Ether", by G. K. Hughes and E. O. P. Thompson.
- "Some Effects of Compression on the Physical Properties of Low-Rank Coal", by J. A. Dulhunty, D.Sc.

Commemoration of Great Scientists.—The following addresses were given:

Simon Stevin (Stevinus), born 1548, by Mr. H. H. Thorne.

Berzelius, died 1848, by Mr. J. B. Thornton.

Important Events in the History of Public Health—Quarantine and the Board of Health established in Venice, 1348, and the First Public Health Act of England, 1848, by Professor Harvey Sutton.

December 1st, 1948.

The six hundred and fifty-sixth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The Vice-President, Mr. F. R. Morrison, was in the chair. Forty-seven members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Geoffrey William Anderson, Leonard Paul Ross.

International Congress of Biochemistry.—It was announced that a circular had been received advising that the International Congress of Biochemistry would be held at Cambridge, England, on August 19th to 25th, 1949.

International Congress of Mathematicians.—It was announced that a circular had been received advising that the International Congress of Mathematicians would be held at Cambridge, Massachusetts, U.S.A., on August 30th to September 6th, 1950.

Library.—The following accessions were received: 176 parts of periodicals and nine purchases.

The following papers were read:

- "Coordination Compounds of Copper. Part I. Complex Copper (II), Cuprates (I)", by C. M. Harris.
- "Mineralogical Examination of Soils Developed on the Prospect Hill Intrusion, New South Wales", by R. Brewer, B.Sc. (Read by title only.)
- "Relations of Rank to Inherent Moisture of Vitrain and Permanent Moisture Reduction on Drying", by J. A. Dulhunty, D.Sc. (Read by title only.)
- "The Chemistry of Bivalent and Trivalent Rhodium. Part XI. The Potential of the Trivalent Quadrivalent Rhodium Couple in Sulphuric Acid", by F. P. Dwyer, D.Sc., and H. N. Schafer, B.Sc.
- "Geology of the North-Western Coalfield, N.S.W. Part VII. The Geology of the Boggabri District", by F. N. Hanlon, D.Sc., Dip.Ed. (Read by title only.)
- "Geology of the North-Western Coalfield, N.S.W. Part VIII. The Geology of the Narrabri District", by F. N. Hanlon, B.Sc., Dip.Ed. (Read by title only.)
- "Note on the Occurrence of Tridymite in Metamorphosed Hawkesbury Sandstone at Bundeena and West Pymble, Sydney District, New South Wales", by G. D. Osborne, D.Sc., Ph.D.
- "The Stratigraphy and General Form of the Timor Anticline, N.S.W.", by G. D. Osborne, D.Sc., Ph.D., A. V. Jopling, B.E., B.Sc., and F. W. Lancaster, B.E., B.Sc.
- "Geology of the Canowindra District, N.S.W. Part I. Stratigraphy and Structure of the Cargo-Toogong District", by N. C. Stevens. (Read by title only.)

Questions.—The following questions were answered:

- "What is the principle of the electron Microscope?" by Mr. R. L. Werner.
- "What was the cause of the change of longitude of Sydney Observatory amounting to some 166 yards in about the year 1932, as indicated by certain one-inch military maps?" by Mr. Harley Wood.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Mr. C. St. J. Mulholland.

Honorary Secretary : Mr. R. O. Chalmers.

Meetings.—Six meetings were held during the year, the average attendance being fourteen members and six visitors.

April 16th.—Address by Mr. F. N. Hanlon on "The Geology of the Willow Tree-Murrurundi District, with special reference to the age of the Werrie Basalts".

May 21st.—Notes and Exhibits : By Miss Quodding : (a) Contact magnetite rich phase with chert, from Prospect ; (b) Crystal models made by pouring molten sulphur into Teclex (a colloidal, flexible moulding material used in dental work). By Mr. Stevens : Three new central western localities for graptolites : (a) two localities near Woodstock ; (b) Cargo. By Mr. C. St. J. Mulholland : "A Review of Recent Work of the Geological Survey." By Mr. H. O. Fletcher : "Recent Fossil Discoveries in Triassic Rocks of the Sydney District." By Mr. R. O. Chalmers : "New Meteorites from New South Wales."

July 23rd.—Exhibit : By Mrs. Sherrard : Specimens of *Monograptus bohemicus* (Barrande) from shale beneath the Dalmanites (Middle Trilobite) bed of the Hume series of the Upper Silurian at Hatton's Corner, Yass, N.S.W.

Address by Dr. Leo Koch : "A New Type of Schedules for Geological and Mineralogical Field Investigations (based on the System of the Categories of Natural Science)." A system of categories has been developed, similar to that of Aristotle's Table of Categories, but worked out as the "System of the Ultimate Modes of Being of Natural Units as Perceived through the Senses". The highest principles of division and grouping of the new system are the forms of apprehension, space and time. The system is called "Tetraktys", because of the fourfold, partly tetrahedral, configuration of its parts and elements.

When the whole content of the "Schedule for the Field Description of Sedimentary Rocks" (*Bull. Am. Assoc. Petroleum Geologists*, Vol. 6, pp. 254-259, 1922) is projected on to forms showing the pattern of the Tetraktys (facts belonging to petrography, mineralogy, palæontology, etc., being projected separately) then approximately half of the categories or categorical concepts of the Tetraktys are covered by corresponding elements of the "Schedule" mentioned above. The "System of the Categories of Natural Science", therefore, when applied to objects of the geological science, shows the totality of the categories of geological field observations possible by means of the unaided senses.

The system can likewise be used for checking the completeness of any other geological and mineralogical features.

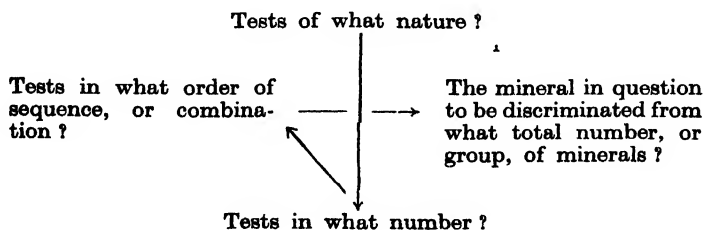
August 27th.—Address by Dr. J. A. Dulhunty : "Some Items of Geological Interest from Abroad."

September 17th.—Address by Dr. G. D. Osborne and Mr. P. B. Andrews : "Structural Data for the Northern End of the Stroud-Gloucester Trough."

November 19th.—Address by Dr. Leo E. Koch : "Use of the Tetraktys (or System of the Categories of Natural Science) in the Process of Mineral Determination."

In a previous address (Koch, 1948, a) the Tetraktys was shown in its application to checking and constructing "schedules" for geological and mineralogical field investigations. In the following address was demonstrated the application of the same system of categories to the whole process of mineral determination.

A critical study into the bulk of the literature on mineral determination published since 1850 revealed that the following four questions, with all their possible mutual combinations and interconnections, are involved in any process of mineral determination :



Answering the complex of these questions in a comprehensive way means to establish a "General Theory of Mineral Determination". Such a theory, apparently, does not exist at the present time.

The Tetraktys can be applied as a general basis for working out systematically the answers to the questions indicated above. The scheme can also be used for plotting and illustrating all constituent elements, phases, and single procedures of the process of mineral determination.

For example, the order of sequence of the different tests used in each particular table recommended for mineral determination can easily be plotted on "forms" showing the pattern of the Tetraktys, and compared with the order of sequence of any other process of mineral determination.

From the study of more than 70 different tables for mineral determination plotted or represented in this way it becomes evident that, in principle, there is no necessity for following strictly a certain distinct order of sequence of the determinative tests. This fact was already empirically proved by the use of punched cards in the process of mineral identification, first recommended by Gray (1920), worked out by Donnay (1935, 1937, 1938), and modified by Hurlbut (1948).

On the other hand, the Tetraktys can advantageously be used in combination with sets of punched cards; this latter method makes it possible to avoid a purely mechanical use, or use at random, of the punched cards for the identification of minerals, by directing systematically the determinative process towards such tests and in such an order of sequence as to guarantee a maximum power of discrimination of the tests selected for the determination.

When expressed in the categorical terms of the Tetraktys, the phenomena produced by blowpipe or wet tests prove to be not different in principle from the so-called external or physical characters recommended in certain types of tables for mineral determination. On the other hand, these "dry" tests for minerals prove to have a particularly strong discriminative power in the determinative process of minerals. This is in accordance with the traditional use of blowpipe tests in the most diverse types of tables worked out for the determination of minerals, even in those which are essentially, or exclusively, based on optical phenomena or methods.

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